TUNGSTEN CLADDING OF TUNGSTEN-URANIUM DIOXIDE (W-UO$_2$) COMPOSITES BY DEPOSITION FROM TUNGSTEN HEXAFLUORIDE (WF$_6$)

(Title Unclassified)

- FINAL REPORT

by

A.W. Hoppe and J.T. Lamartine

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
UNDER CONTRACT NAS 3-5218

Astronuclear Laboratory
Westinghouse Electric Corporation

N73-70996   Unclas
00/99   53536

(NASA-CR-54835) TUNGSTEN CLADDING OF
TUNGSTEN-URANIUM DIOXIDE (W-UO2)
COMPOSITES BY DEPOSITION FROM TUNGSTEN
HEXAFLUORIDE (NF6) Final Report, 26
Jun. (Westinghouse Electric Corp.) 84 p

(PAGES)   CR 54835
(NASA CR OR TMX OR AD NUMBER)

(CODE)   17
(CATEGORY)

NOTICE

The report was prepared as an account of Government sponsored work. Neither the United States, nor the National Aeronautics and Space Administration (NASA) nor any person acting on behalf of NASA:

    A.   Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

    B.   Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

As used above, "person acting on behalf of NASA" includes any employee or contractor of NASA, or employee of such contractor, to the extent that such employee or contractor of NASA, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with NASA, or his employment with such contractor.

Requests for copies of this report should be referred to:

National Aeronautics and Space Administration
Office of Scientific and Technical Information
Attention: AFSS-A
Washington, D. C.   20546

$C\mathcal{E}6$-00917

**(W) Astronuclear
Laboratory**
WANL-PR(Z)-003
NASA CR-54835

TUNGSTEN CLADDING OF
TUNGSTEN-URANIUM DIOXIDE (W-UO$_2$) COMPOSITES BY DEPOSITION FROM TUNGSTEN HEXAFLUORIDE (WF$_6$)
(Title Unclassified)

by

A. W. Hoppe

and

J. T. Lamartine

FINAL REPORT

Covering the Period

June 26, 1964 to June 26, 1965

Prepared For

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Contract NAS 3-5218

Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Materials and Structures Division
Robert M. Caves, Project Manager

Astronuclear Laboratory
Westinghouse Electric Corporation
Pittsburgh 36, Pa.

INFORMATION CATEGORY
CONFIDENTIAL-RD

1-10-66

Authorized Classifier   Date

ABSTRACT

5048/

A program was conducted to develop a process for cladding tungsten cermet fuels with tungsten deposited from the vapor state by the hydrogen reduction of tungsten hexafluoride.

It was shown that the rate of deposition of tungsten from WF_6 and the uniformity of the deposit can be controlled in a reproducible manner by exercising control over the deposition parameters. High temperature fuel retention testing of tungsten clad $W-UO_2$ at $4500^\circ F$ ($2480^\circ C$) in hydrogen for two hours has demonstrated that the vapor deposited layer retains its high density and high integrity and that it effectively and consistently restricts fuel loss.

Conf/RD   author

W Astronuclear
Laboratory

TABLE OF CONTENTS

SUMMARY

The NASA-Lewis Research Center is studying the feasbility of a water moderated nuclear reactor for space propulsion. This reactor, which will use a tungsten-uranium dioxide ($W-UO_2$) dispersion fuel and hydrogen gas propellant, is expected to operate at temperatures up to 5000°F (2760°C) for times of at least 2 hours. To preclude gross fuel losses at operating temperature due to the high vapor pressure of UO_2, the intricate fueled bodies will be clad with a thin layer of tungsten. To this end, a program was conducted at the Westinghouse Astronuclear Laboratory to develop a process for cladding $W-20$ v/o UO_2 composites with vapor deposited tungsten by reducing tungsten hexafluoride gas (WF_6) with hydrogen. Efforts at WANL were directed toward optimizing deposition process parameters to attain control of qualities such as coating thickness, uniformity, density, impurity content, and surface quality. Substrate preparation methods were investigated in the interest of completely eliminating the interface between the fueled substrate and cladding. In addition, the effects of process parameters and post-cladding heat treatments on the fuel retention properties of clad composites at 4500°F (2480°C) in hydrogen for 2 hours were evaluated.

As a result of work performed during the program, it has been shown that the rate of deposition of tungsten from WF_6 and the uniformity of the deposit can be varied in a predictable and reproducible manner by exercising control over the temperature, pressure, and gas flow rates at which the deposits are produced. Although both deposition rate and deposit uniformity are influenced by deposition chamber geometry, it has been demonstrated that deposits of over 98% density and of nearly identical quality may be produced on substrates heated either by radiation in a hot wall chamber or by RF induction in a cold wall system with only minimal experimentation being required to transfer technology from one system to the other after proper control of the temperature gradient is achieved on induction heated specimens.

A significant result of the study is the discovery that substrate nucleation and epitaxial growth in deposits made on both unfueled tungsten and $W-UO_2$ substrates may be effected by pre-treating the substrates in hydrogen at 1600°F (870°C) and 15 mm Hg abs. pressure in the deposition chamber prior to coating. Substrate nucleated deposits of this type have been observed to survive bend testing around a 0.025" radius at room temperature, 800°F (430°C), and 1000°F (540°C) without separation at the substrate-clad interface. Additional work in the area of bonding and deposit structure has revealed that the structure of deposits on $W-UO_2$ may be altered by recrystallization and that bonding may be improved, as a result of grain growth across the inter-face, by post-deposition heat treatment at 3600°F (1980°C) for 15 minutes in a vacuum of 10^{-6} mm Hg.

High temperature fuel retention testing of tunsten-clad, $W-UO_2$ at 4500°F (2480°C) in hydrogen for 2 hours has demonstrated that the vapor deposited layer effectively and consistently restricts fuel losses to less than 0.15 mg/cm^2 (0.21% of contained UO_2). Microporosity, which

had been observed in the cladding (deposited at temperatures below approximately $1100^\circ F$ ($595^\circ C$)) after exposure to the environmental test, was thought to be caused by low levels of fluorine in the clad. This microporosity (normally observed after the high temperature test) was reduced or eliminated in deposits produced at temperatures up to $1295^\circ F$ ($700^\circ C$) and also in deposits that received post-deposition heat treatment at $3600^\circ F$ ($1980^\circ C$) for 1 hour at 10^{-6} mm Hg. Fueled tungsten substrates clad at $1148^\circ F$ ($620^\circ C$) showed that no pores formed in the cladding after 2 hours exposure in hydrogen at $4500^\circ F$ ($2480^\circ C$). Removal of UO_2 particles exposed to the surface of the $W-UO_2$ composites by dissolution in HNO_3 prior to cladding to preclude a reaction between the fuel and HF (the product of WF_6 reduction) appears to offer no advantage to improving fuel retention performance in the retention test environment.

INTRODUCTION

The NASA-Lewis Research Center is studying the feasibility of a water-moderated nuclear reactor for space propulsion. The reactor, which will use a tungsten-uranium dioxide ($W-UO_2$) dispersion fuel and hydrogen gas propellant, is expected to operate at temperatures up to $5000^\circ F$ ($2760^\circ C$) for times of at least 2 hours. To preclude gross fuel losses at operating temperature due to the high vapor pressure of UO_2, the intricate fueled bodies may be clad with a thin layer of tungsten.

To minimize the heat transfer path between fuel and coolant and to reduce the amount of inert structural material in the reactor core, thin cladding is desirable. Cladding thickness of 0.001" to 0.005" could be applied to plates or cylinders as mechanically added sheet or tubular material which could be gas-pressure bonded (or roll bonded in the case of flat plates) to the cermet core. Thin cladding materials in the range of 0.0005" to 0.002", however, would be difficult to apply by this method on more complex shapes. Since presently known cladding methods are applicable to only rather simple shapes, it is mandatory that suitable methods be developed for coating thin, more complex configurations. It is desirable that this cladding satisfy the following minimum requirements.

1. The clad must exhibit a pore-free metallurgical bond to the substrate without the prior interface being discernible.

2. The cladding must be useful up to $5000^\circ F$ ($2760^\circ C$) without spalling, cracking, or blistering, and must withstand at least 10 cycles to $4500^\circ F$ ($2480^\circ C$), with a total time at temperatures of at least two hours.

3. The coating thickness variation must be within a one-half mil tolerance for thin claddings (less than 0.001") and a one mil tolerance for thicker layers (greater than 0.001").

4. The coating shall be of high purity with no single impurity greater than 50 ppm, and no more than 10 ppm each of the following elements: C, O, S, Be, B, Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sn, and Pb. Total halide content shall not exceed 15 ppm.

5. The coating shall completely encapsulate the $W-UO_2$ composite and shall have a minimum density of 18.7 g/cc.

6. The coating shall inhibit volatilization of the UO_2 by limiting the UO_2 loss, after two hours in flowing hydrogen at $4500^\circ F$ ($2480^\circ C$), to an amount less than 1 mg/cm^2 of surface area.

To this end, a program was conducted at WANL to develop a process for cladding W-20 v/o UO_2 composites with vapor deposited tungsten by reducing tungsten hexafluoride gas (WF_6) with hydrogen.

It is known that tungsten may be deposited from the vapor state from any of several different tungsten compounds[1]. Tungsten carbonyl, for example, has been used to successfully yield high quality deposits. Coatings deposited from the carbonyl, however, have been reported to have a higher impurity content, particularly with respect to carbon, than is considered desirable[2]. Tungsten hexachloride has also been used but requires special equipment for volatilization of the solid chloride prior to injection into the vapor deposition chamber. The WF_6 compound is easily vaporized at room temperature and can be secured with a relatively high degree of purity. The temperature range for the deposit is not as high nor as critical in its control as the temperature range for deposition from other compounds. These qualities result in a high-density, high-purity deposit[3,4,5,6,7] that should be quite suitable for cladding $W-UO_2$ fuels.

Although much work has been done with the hexafluoride process, most of it has been oriented toward the production of tungsten particles and free standing tungsten shapes on expandable mandrels. No standard or best processing procedures presently exist since the process has been employed for widely varying uses and each experimenter has chosen parameters that meet his needs and equipment capabilities. Although some preliminary work had been done on tungsten coated $W-UO_2$[1], direct application of most of the existing technology to cladding fueled compacts was thought not to be possible when this program was initiated. Many questions unique to this application remained to be answered. For example, the adherence of tungsten deposits to fueled compacts had never been adequately demonstrated. Another area of question was whether a reaction between HF, the by-product of WF_6 reduction by hydrogen, and the UO_2 would occur during the early stages of deposition[8] and whether this reaction, if it occurred, would influence the performance of the clad fueled compact in the high temperature, hydrogen reactor environment. Little was reported about specific effects of substrate surface preparation, deposition temperature, reactant flow rates, and reaction pressures on such deposit properties as grain size, deposition rate, deposit density, deposit purity, and adherence.

The program conducted at Westinghouse was divided into two phases; the first, a demonstration of the feasibility of cladding by this method and the optimization of the coating process; the second, the cladding of fueled samples for environmental testing. Efforts, under Task I, were directed toward optimizing deposition process parameters to attain control of qualities such as coating thickness, uniformity, density, impurity content, and surface quality. Substrate preparation methods were investigated in the interest of completely eliminating the interface between the fueled substrate and cladding. In addition, the effects of process parameters and post-cladding heat treatments on the fuel retention properties of clad composites at 4500°F (2480°C) in hydrogen for 2 hours were evaluated. For Task II, the deposition equipment was modified to improve the reliability and a continued investigation of process parameters showed that cladding which retained high integrity at elevated temperature could be readily reproduced for coating large quantities of experimental samples.

DESCRIPTION OF EQUIPMENT AND MATERIALS

Deposition System

A schematic of the vapor deposition apparatus used at Westinghouse is presented in Figure 1. Perusal of the schematic reveals that an induction heated deposition chamber and a resistance heated deposition chamber are available in alternate pieces of equipment, each of which have equivalent gas ducting. With this arrangement, metered flows of hydrogen and WF_6 may be simultaneously injected into the deposition chamber of either apparatus where they react to deposit tungsten on a heated sample. After passing through the deposition chamber, the gases flow through a stripping chamber maintained at $1835°F$ ($1000°C$) where the $H_2 + WF_6$ reaction is completed thus removing the balance of the tungsten from the WF_6 vapor. The vacuum pump shown in the system is used to maintain the system at the desired operating pressure. The cold trap between the pump and stripping chamber is maintained at $-115°F$ ($-80°C$) with dry ice and alcohol to preclude back streaming oil vapors entering the deposition chamber and contaminating the tungsten deposit. The gases are exhausted from the pump through a counter-current, water scrubbing column filled with alumina balls where HF, the reactor product, is removed from the stream. Finally, the exhaust hydrogen is burned.

The pressure in the system is monitored with the mercury manometer shown in the schematic. The special arrangements of metering valves, flow meters, and pressure gauges shown in each flow train permit metering the gases at the conditions for which the flow meters were calibrated, viz, $75°F$ and 1 atmosphere.

Special precautions have been taken with the design of this system to maintain lowest possible levels of contamination in the gas stream. Air is excluded from the stream by maintaining the system vacuum leak tight to helium. Hydrogen gas purity is maintained by passing the stream through a palladium catalyst, a drying column, and a liquid nitrogen cold trap before injecting it into the deposition chamber. Although commercial WF_6 is relatively pure, it still contains some undesirable impurities that may be transmitted to the tungsten deposit. All WF_6 cylinders, therefore, are purified by immersing in a dry ice and acetone bath to freeze the WF_6 and evacuating to less than 200 microns to remove volatile impurities. Other steps taken to assure deposit purity are extensive use of copper and stainless steel for piping and chambers and the use of an inert thermoplastic hydrofluorocarbon flowmeter in the WF_6 gas metering train instead of a conventional borosilicate glass flowmeter that is attacked by and contaminates the WF_6. All other components are standard, commercially available items.

For Task II, the deposition equipment was modified to improve the leak tightness, reduce the number of joints, improve the pumping capability to permit lower coating pressures, and to make some sections easily replaceable. Expendable liners were used in the deposition chamber to prevent tungsten deposits on the hot wall from constricting the useful diameter.
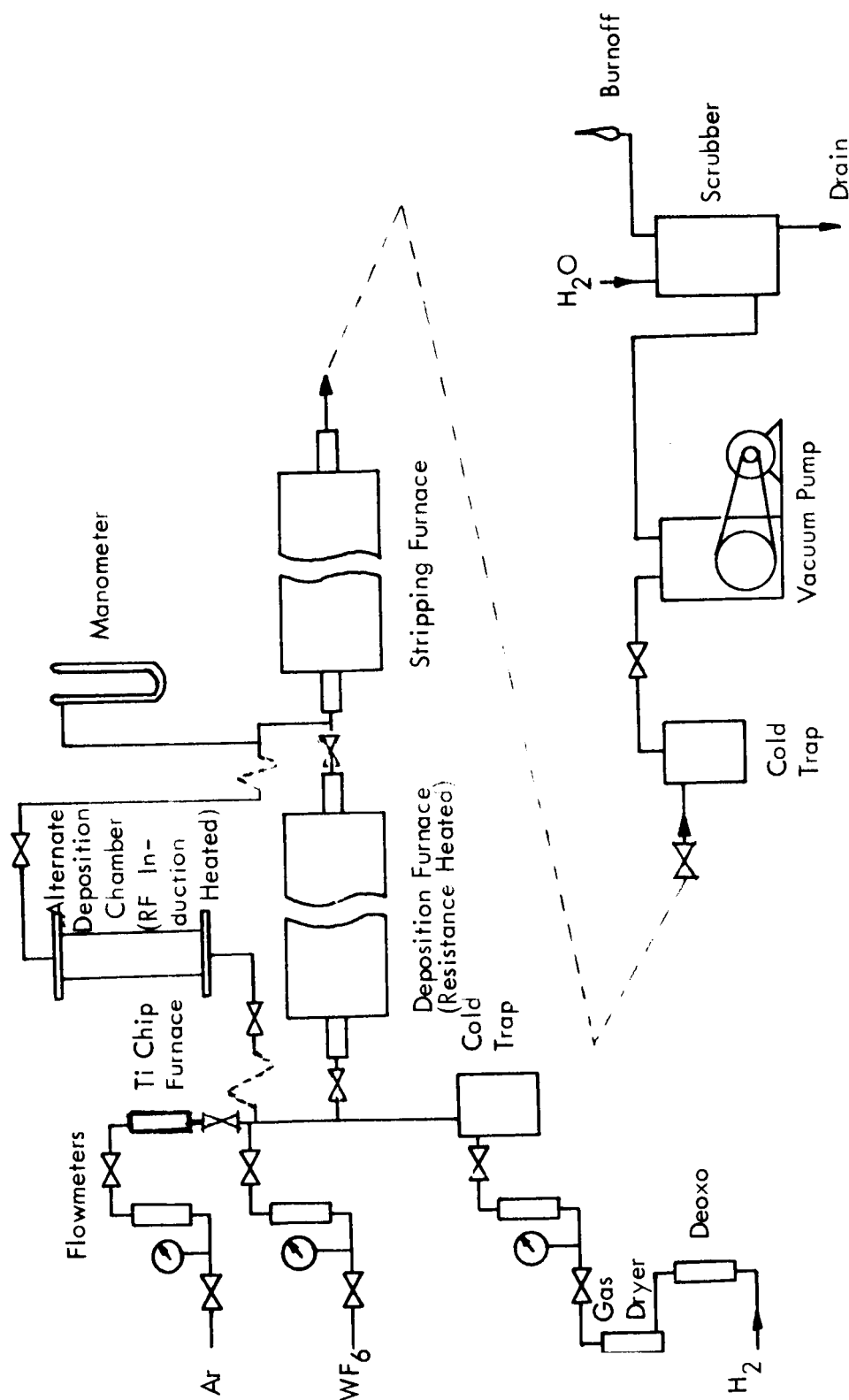
Astronuclear
Laboratory

FIGURE 1: Schematic of Tungsten Deposition Apparatus

6

 Astronuclear
Laboratory

Support Systems

As shown in Figure 2, several sample support systems have been employed in the coating work done in the resistance heated deposition chamber.

The first system, Figure 2A, consisted of a copper frame with two horizontal copper wires on which to support the 3/4" wide by 3" long unfueled tungsten sample. Deposits made on substrates supported in this manner were consistently of greater thickness on the upper surface than on the downward surface. In addition, the two support wires, although only about 20 mils thick, caused sufficient disruption of the gas flow to shadow the downstream portions of the sample with the result that gross nonuniformities in deposit thickness occurred.

In system two, Figure 2B, the sample was held vertically by three wires in the same copper frame. Deposits produced using this system exhibited good uniformity side-to-side and end-to-end but were prone to shadowing effects on the lower corner of the downstream end due to disruption of the flow in this area by the support frame.

The system shown in Figure 2C is a further improvement. The samples were supported vertically by 10 mil tungsten wire strung through a half section of 1-1/8" diameter copper tube. Deposits made on samples supported in this manner exhibit over-all uniformity on the order of $\pm 1/2$ mil and shadowing does not occur. The most recent modification in Figure 2D replaced the half section of copper tube with two small diameter stainless steel tubes from which wire slings were suspended to hold the sample in a vertical position similar to that shown. In addition to supporting the samples, the stainless steel tubes were used to hold monitoring thermocouples. One problem still remaining and one which will always remain with any system using static supports for depositing thin films, is that very small uncoated areas are sometimes left where the tungsten support wires contact the substrate. Mobile support systems studied but not installed because of insufficient time included a rotating sample basket, a series of rollers to move the samples, and a vibrator or eccentric cam actuated oscillating support using either pins or slings.

The support system used in the induction heated deposition system is illustrated in Figure 3. This support was comprised of a double teflon spider that formed a tight fit in the vycor tube, on Al_2O_3 rod, and a tungsten wire hook. A small hole was drilled through one end of the sample with micro abrasive blast equipment. The sample was then supported vertically in the chamber from the tungsten hook. During deposition, the sample remained stable and the uniformity of the deposit was not influenced by the support members. Furthermore, since the support components were not heated, either radiantly or inductively, reduction of WF_6 occurred only on the heated sample.

High Temperature Fuel Retention Test System

A schematic of the apparatus used for evaluating the fuel retention properties of tungsten clad $W-UO_2$ at 4500°F (2480°C) in flowing hydrogen is depicted in Figure 4. As shown in the drawing, this apparatus is essentially a water cooled copper current concentrator enclosed in a vycor pipe and end plate housing. Hydrogen or helium is admitted to the system through the top plate and exhausted through the bottom plate to a two stage oil filled trap designed to remove

A.

B.

C.

D.
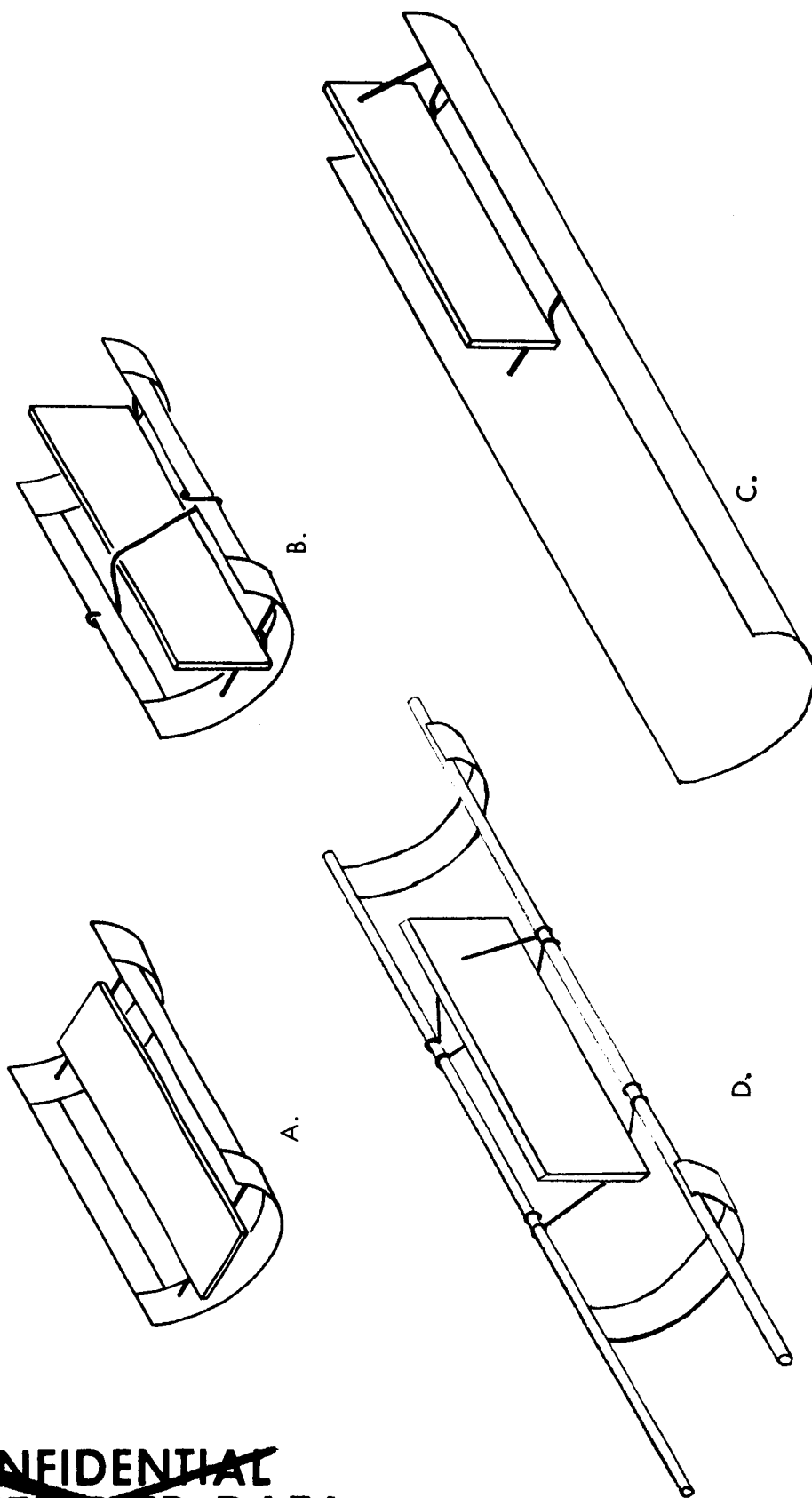
FIGURE 2   Sample Support Systems,
Resistance Heated Systems

Astronuclear
Laboratory

VYCOR DEPOSITION
CHAMBER

TEFLON SPIDER

Al_2O_3 ROD

SEE DETAIL "A"

RF INDUCTION
COIL

SAMPLE

TUNGSTEN WIRE HOOK

DETAIL "A"
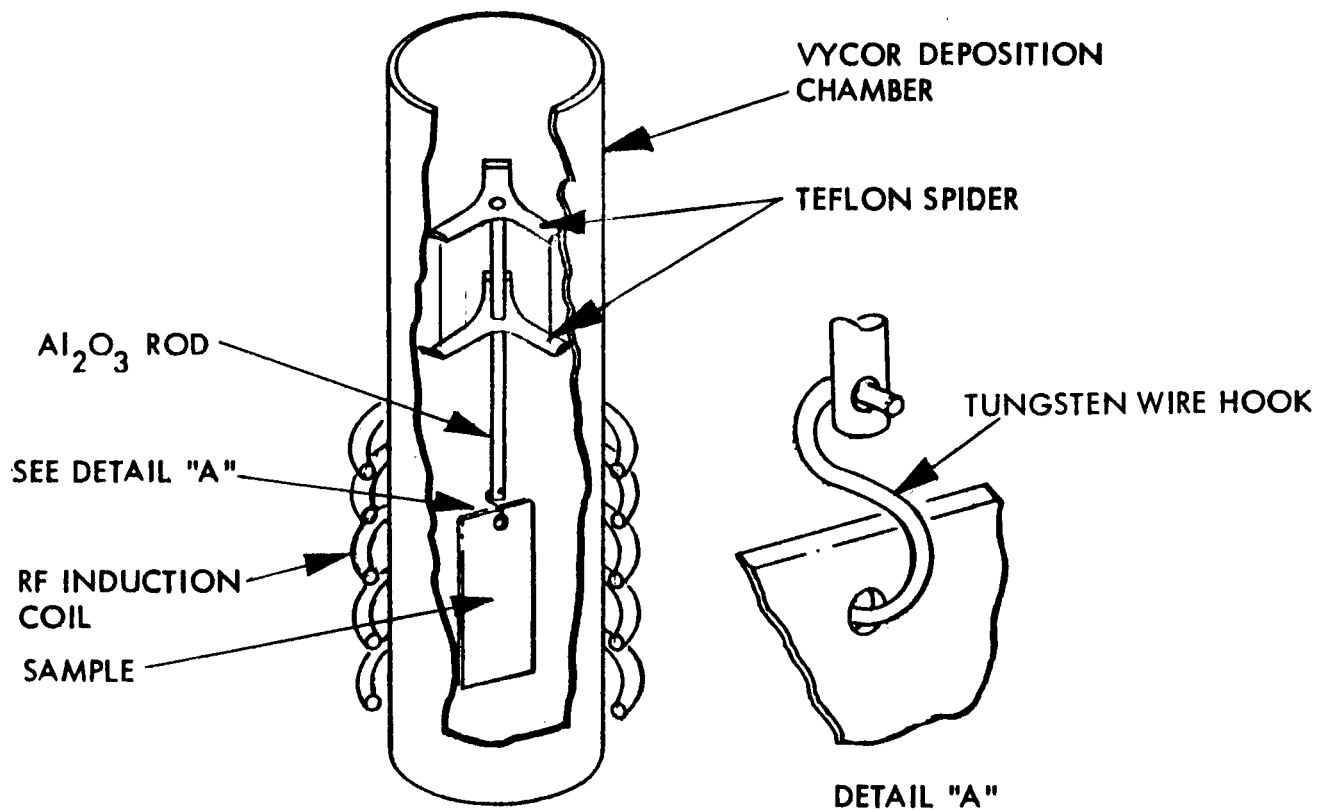
603395A

FIGURE 3

Support System Used in Induction Heated Deposition Chamber
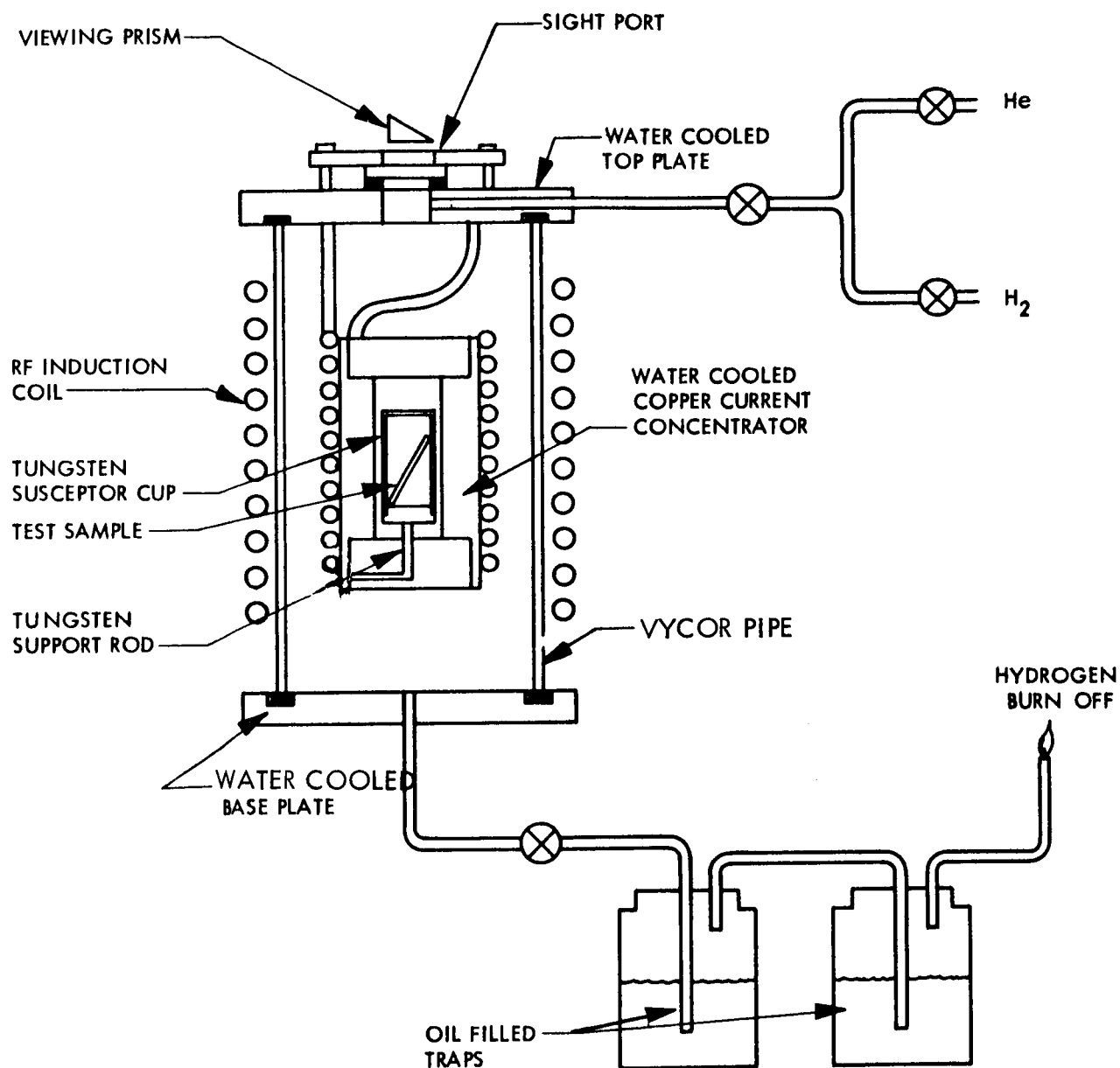
FIGURE 4

Schematic of High Temperature Fuel Retention Test Apparatus

entrained uranium. The sample under test rests in a tungsten susceptor cup which is covered, top and bottom, with tungsten washers to promote temperature uniformity.

The system is powered by a 50 KW, 350-400 kc RF generator. The temperature of the sample is measured through the sight port in the top plate with a standard optical pyrometer. It was established that black body conditions prevailed within the susceptor cup by experimentation with a black body hole. Corrections for transmission losses through the viewing window and prism were made.

Materials

Hydrogen - Standard, commercially available bottled hydrogen was used for all phases of the work. As described above, the hydrogen used in deposition work was passed sequentially through a palladium catalytic deoxygenizing cell, a drying column and a liquid nitrogen cooled cold trap. Hydrogen for the fuel retention test apparatus was taken directly from the producers cylinder without additional purification.

Helium - Helium was used exclusively in the sample cool down phases of high temperature fuel retention testing. As such, it was taken directly from the cylinder.

Argon - Standard commercial argon was used, as delivered from the suppliers cylinder, for those phases of the deposition program requiring a carrier gas. It was also used to purge the evacuated deposition system prior to starting hydrogen flow and furnace heating. For the last phase, a titanium chip purification furnace was added to the system.

Tungsten Hexafluoride - This material was purchased in 20 pound cylinders. As described above, each cylinder of WF_6 was purified by freezing in a mixture of dry ice and alcohol and then evacuating to less than 200 microns of mercury to remove volatile impurities. An analysis of the WF_6 in two typical cylinders after purification is presented in Table I.

Tungsten Sheet - Tungsten strip, 3/4" wide x 0.032" thick, rolled from powder metallurgy stock was purchased in the hot rolled and pickled condition. To simulate the structure of fueled material as closely as possible, the strip was cut into 3" lengths and recrystallized at 3600°F (1980°C) for 10-20 minutes at 10^{-6} mm Hg.

Tungsten-UO_2 Samples - For experimental work in Task I, thirty-two 3/4" x 3" x .020" plates of W-20 v/o UO_2 were supplied by NASA-Lewis Research Center in two batches; twelve in one, twenty in the other. Visual and other examinations revealed slight differences between plates from the two batches. The surfaces of the 20 plates in batch 1 were observed to be somewhat rough and light brown in color with occasional areas of even darker color. All of the twelve plates in batch 2 were smooth and metallic bright. The unit cell dimension of UO_2 in plates from batch 1 has been measured by x-ray diffraction (procedure described in Appendix I) and found to be on the order of 5.426 Å for surface exposed UO_2 and 5.47 Å (theoretical value is 5.468 Å) for UO_2 within the interior of the compacts.

TABLE I

ANALYSIS OF TUNGSTEN HEXAFLUORIDE

Concentration (ppm)

Impurity	Cylinder No. 1	Cylinder No. 2
Ca	9	4
Fe	11	1.7
Mg	0.8	0.5
Ni	0.9	1.0
Si	6.2	5.0
Al	< 1	< 1
B	< 0.5	< 0.5
Cd	<15	<15
Co	< 1.5	< 1.5
Au	1.0	< 0.5
Mo	< 1.5	< 1.5

The constricted lattice of UO_2 at the plate surface is indicative of either excess oxygen or the presence of other impurities within the UO_2. Attempts to reduce excess oxygen from the surface UO_2 by treating the composites in dry hydrogen at temperatures to 2820°F (1550°C) for as long as 24 hours resulted in little or no change in lattice parameters. X-ray fluorescence studies revealed that trace qualities of zirconium were present in the surface layers of the composites but were not present in the interior. It was, therefore, concluded that zirconium, introduced in the fabrication process as ZrO_2 sintering barriers, was responsible for the observed UO_2 lattice constrictions. Similar x-ray work with the batch 2 compacts revealed a lesser degree of lattice constrictions and reduced zirconium peaks on the surface layers.

Additional W-UO_2 substrate samples were furnished for coating in Task II prior to environmental testing. The samples included plates similar in size to those described above, tensile specimens 3/4" x 7" x .020", and cylinders which were .500" I.D. x .545" O.D. x 1" long.

EXPERIMENTAL PROCEDURES

Efforts under Task I of the contract were directed toward optimizing parameters of the coating process to attain control over such qualities as deposit thickness, uniformity, density, imperviousness, impurity content, rate of build-up, and surface quality. In the interest of completely eliminating the interface between the cermet substrate and the tungsten cladding, substrate preparation methods and post deposition heat treatments were evaluated. To obtain a uniform, integral coating on all surfaces of the substrate, several methods of supporting specimens were evaluated. Finally, the fuel retention properties of continuous tungsten coatings deposited on W-20 v/o UO_2 compacts were evaluated by testing in hydrogen at 4500°F (2480°C) for two hours. In Task II, the deposition parameters were further investigated to improve the integrity of the cladding at 4500°F (2480°C) prior to selection of optimum parameters for coating the quantity of specimens required for final environmental testing.

To attain these ends, initial deposits were made on recrystallized, unfueled tungsten substrates in the resistance heated system described above. Temperatures and pressures in the range 660°F to 1295°F (350°C to 700°C) and 3 to 360 mm Hg were investigated. Hydrogen to WF_6 ratios of 3.3:1 to 150:1 were utilized. Optimum parameters within the above ranges were developed for cladding unfueled tungsten by systematically varying each parameter followed by an evaluation of the resultant deposit. For this portion of the program, deposit evaluation typically consisted of micrometric measurements for thickness and uniformity and metallographic examination to define the deposit microstructure.

Concomitant with these studies, the effects of substrate preparation on the nature of the bond between substrate and cladding were considered. Predeposition substrate preparation that were evaluated consisted of the following:

1. Degreasing with acetone.
2. Etching in a solution of 40% Hf-60% HNO_3 to remove 0.001" per side.

3. Oxide reduction treatment in the deposition chamber at 1600°F (870°C) in hydrogen for 15 minutes at about 15 mm Hg absolute pressure.

4. Etching in 40%HF-60%HNO_3 per (2) followed by the hydrogen reduction treatment described in (3).

Deposits which were made on substrates pretreated by the above methods were evaluated metallographically to define the nature of the bond. The relative adherence of the deposit to the substrate was demonstrated by the ability of the deposit to survive abrasive disc sectioning or bending around a 0.025" radius at temperatures from room temperature to 1000°F (540°C).

In addition to establishing the relationship between substrate preparation and bonding, the effects of post deposition thermal treatment on enhancement of the clad-substrate bond were studied. Unfueled tungsten samples clad under a wide range of parameters, following pretreatment per the four methods outlined above, were given either a 15 minute or a 1 hour thermal treatment at 3600°F (1980°C) at 10^{-6} mm Hg and subsequently evaluated metallographically to detect improvements in the nature of the interface or deposit structure.

At this juncture, the applicability of the parameters and processes developed with plain tungsten to cladding the NASA supplied W-20^v/oUO_2 composites was demonstrated. In addition, studies were performed in which both fueled and unfueled samples were clad in the RF induction heated system to define the applicability of procedures and parameters developed with the resistance heated system.

The fuel retention test program, which was conducted in the apparatus shown in Figure 4, was designed to evaluate the effects of deposition parameters, precladding surface treatments, and post cladding thermal treatments on the fuel retention properties of clad, NASA supplied, W-20^v/o UO_2 composites. All of the samples tested were clad in the resistance heated system. Fuel retention testing was performed for 2 hours at 4500°F (2480°C) in flowing hydrogen according to the following plan:

1. Load the weighed and measured samples into the system, purge with helium for 5 minutes minimum then purge with hydrogen for 5 minutes minimum.

2. Heat to 3000°F (1650°C), 2 minutes to temperatures and hold for 30 minutes. Cool to room temperature in helium.

3. Weigh and measure samples.

4. Load samples into system. Purge with He and H_2 per step (1).

5. Heat to 4500°F; time to temperature 1 minute. Hold 2 hours.

6. Cool to 2000°F (1095°C) in H_2. Purge system with He.

7. Cool from 2000°F (1095°C) to room temperature in He.

Tested samples were weighed and measured to define weight and dimensional changes, sectioned, and examined metallographically to evaluate changes in microstructure. In addition, several samples were bend tested at 1000°F (540°C) to evaluate post test cladding adherency.

RESULTS

The results of experimental work performed during both phases of the contract are discussed in the following sections.

Deposition Rate

The basic parameters that define and control the pyrolytic deposition of tungsten from WF_6 are temperature, pressure, WF_6 flow rate, and hydrogen flow rate. Of these four parameters it has been found that temperature and pressure exhibit the greatest influence on the rate at which tungsten is deposited on the substrate. It was also found that the relationship of these parameters is sensitive to the characteristics of the deposition equipment.

The rate of tungsten deposition as a function of system pressure for one apparatus is illustrated in Figure 5. As shown in this graph, the rate of build-up of pyrolytic tungsten at 915°F (490°C) appears to exhibit a logarithmic dependency on the pressure at which the deposit is made. From the structural standpoint, thin deposits made at low pressures exhibit the same microstructure as deposits made at high pressure. No voids or microporosity were observed in the as deposited condition at magnifications up to about 500X in any of the deposits regardless of deposition pressure within the range studied.

The effects of pressure on deposition rate are further illustrated in Figure 6 which shows the interrelationship between temperature and deposition rate as determined in the early resistance heated system at average system pressures of 20 mm and 40 mm of Hg. At both pressures, the deposition rate increases linearly with temperature over the range of temperatures investigated. Comparison of the two curves reveals that at the lower pressure the effect of temperature on the rate of deposition is reduced. This observation has at least two important implications. First, extrapolation of the two curves to zero deposition rate indicates that the minimum temperature at which deposition will occur may be lowered by operating the system at lower pressure. Secondly, low system pressure allows greater control over deposit thickness at higher deposition temperatures.

Metallographic examination has shown that thin deposits produced in this study appear to be identical in nature regardless of deposition rate. All deposits appeared to be dense with no entrapped voids or microporosity. Experience with one sample coated at 1185°F (640°C) and 40 mm Hg has indicated that, at rates greater than 16 mils/hour, growth becomes markedly dendritic and results in the entrapment of voids between the dendrites. This sample was not included in the data presented in Figure 6 because the system used to support the substrate influenced the thickness of the deposit. One difference between deposits made at high and

low deposition rates has been observed. In the interest of clarity of presentation, this observation will be discussed in the section concerning surface preparation and crystal growth.

It has been observed that the rate of tungsten deposition in the RF induction heated system falls within the range predicted by the data presented in Figures 5 and 6. Rate versus temperature is illustrated in Figure 7. As shown in the graph, deposition rate in the induction heated system varied as a linear function of temperature. As predicted from the pressure relationship graph shown in Figure 6, the experimental curve for induction heating at 27 mm Hg system pressure falls on the theoretical point.

Reproducibility

It has been determined that at any given set of operating parameters (pressure, temperature, and measured flow rates) tungsten deposits of predetermined thickness may be consistently produced provided allowances are made for increases in the linear flow rate induced by changes in the cross section of the heated deposition chamber as subsequent depositions reduce its diameter. Experience gained from over 90 deposition runs indicates that as the diameter of the resistance heated deposition chamber decreases, the rate at which tungsten is deposited increases. No specific measure of this effect has been made; however, it can be illustrated by review of the data presented in Table II. From the data of runs 62 through 65, it can be seen that the deposition rate was relatively constant at about 1.5 mils per hour at a deposition temperature of 896°F (480°C). In runs 66 through 68, rather heavy deposits were made at a higher temperature causing a reduction in the chamber diameter as tungsten was deposited on the hot walls. As the chamber diameter became constricted during these three runs, the deposition rate, at 535°C, increased from 2.5 to 6.0 mils/hour. Following these heavy deposits, deposition was again continued at 896°F (480°C); however, chamber constriction had caused the rate to increase to about 2.3 mils/hour. It is difficult to make qualitative measures of the change in deposition rate with deposition chamber constriction because of other, non-measurable, attendant effects such as warping of the muffle and copper boat as the deposited layers increased.

This shift in deposition rate, on the other hand, does not present a significant problem to ones ability to reproducibly deposit tungsten layers of desired thickness. Once the basic rates have been established for a set of operating parameters, thickness control may be maintained by basing the deposition rate for any run on the rate calculated from the preceding run. The degree to which deposit thickness was controlled in this way for Task I is demonstrated by the data presented in Table III.

This problem does not exist with the induction heated system since tungsten is not deposited on the cold chamber walls. In addition, this problem was essentially eliminated in Task II with the modified radiantly heated deposition chamber which used replaceable liners to prevent constriction of the coating chamber. The data in Table IV illustrates the reproducibility of samples produced in quantity for final evaluation.
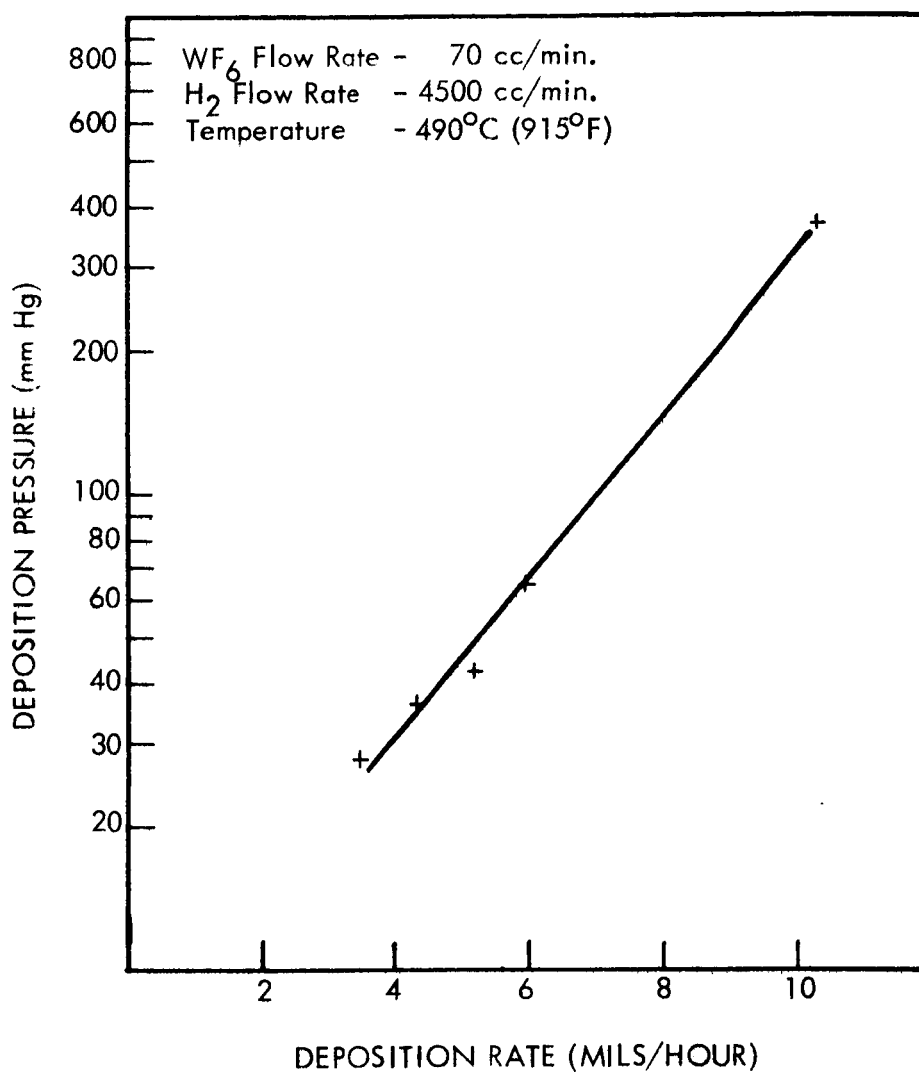
Astronuclear
Laboratory

FIGURE 5

Pyrolytic Tungsten Rate as a Function of Pressure at Constant
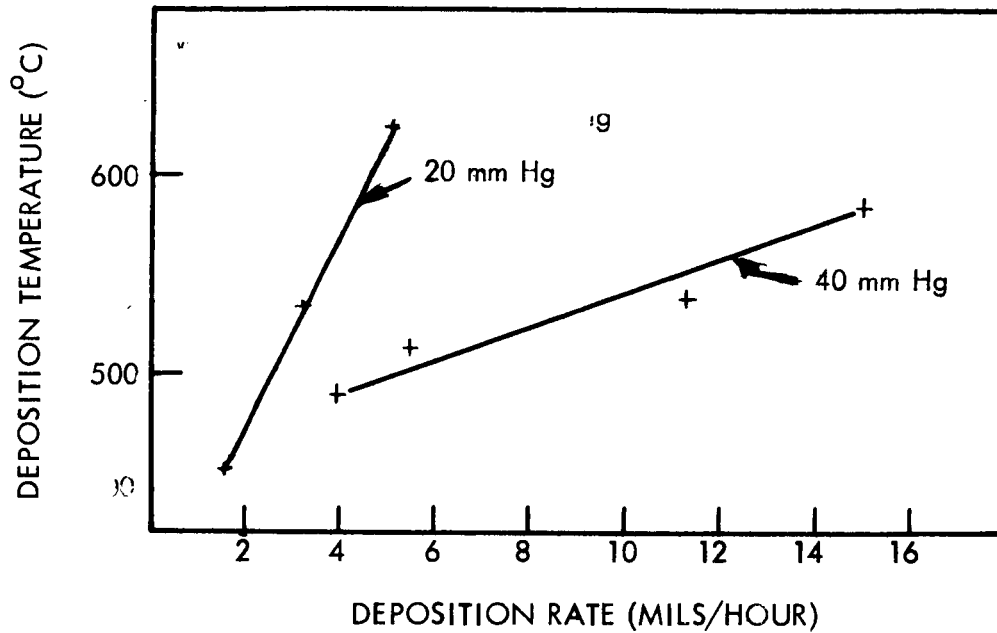Temperature and Flow Rate for Resistance Heated System

FIGURE 6

Pyrolytic Tungsten Deposition Rate as a Function of Deposition
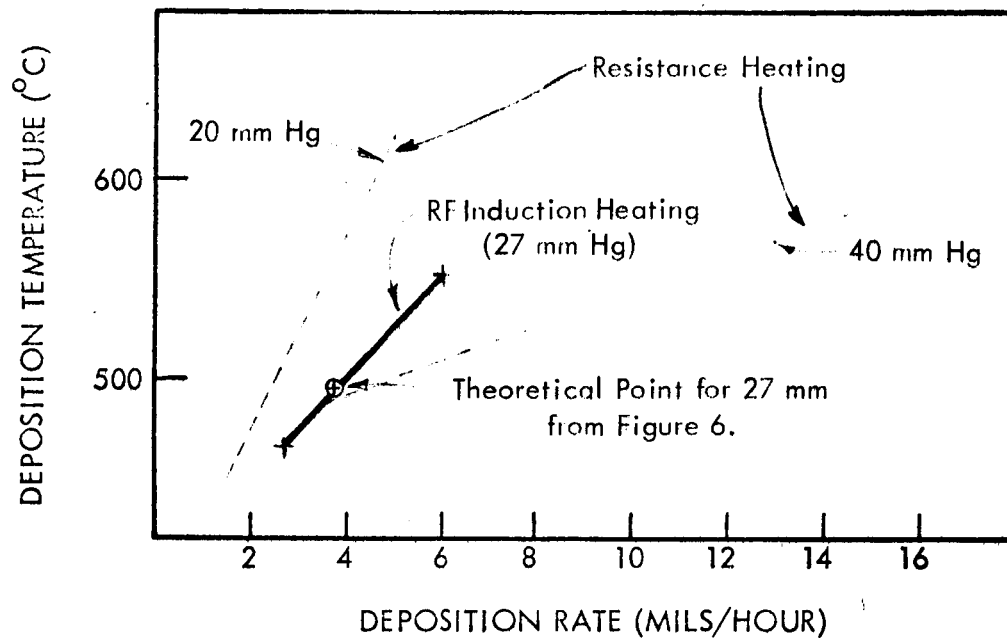Temperature and Pressure for Resistance Heated System

FIGURE 7

Pyrolytic Tungsten Deposition Rate as a Function of Deposition
Temperature and Pressure for Induction Heated System

Astronuclear
Laboratory

TABLE II

VARIATION OF DEPOSITION RATE WITH BUILD-UP
OF DEPOSITS ON DEPOSITION CHAMBER WALLS

Run No.	Deposit Thickness (mils)	Deposition Temp. $^\circ C$	Deposition Time (min.)	Average Deposition Rate (mils/hr)	Deposition Chamber Diameter Change (mils from Run 62)
62	0.5	480	20	1.5	0
63	0.9	480	35	1.58	-1
64	1.7	480	65	1.57	-2.8
65	1.55	480	65	1.42	-6.2
66	17.5	535	420	2.5	-9.3
67	32	535	425	4.5	-44.3
68	18	535	180	6.0	-108.0
69	3.4	480	60	3.4	-144.0
70	1.2	480	35	2.1	-146.5
71	1.6	480	40	2.3	-149.5
72	1.6	480	40	2.3	-152.5

Astronuclear
Laboratory

TABLE III

REPRODUCIBILITY OF PROCESS
(TASK I)

Run Number	Desired Thickness (Mils)	Range of Actual Deposit Thickness (Mils)
73	0.5 – 1.0	0.55 – 0.80
74	0.5 – 1.0	0.45 – 0.60
75	0.5 – 1.0	0.75 – 0.90
84	0.5 – 1.0	0.85 – 1.15
87	0.5 – 1.0	0.75 – 0.95
80	1.0 – 2.0	1.0 – 1.4
81	1.0 – 2.0	1.1 – 1.55
83	1.0 – 2.0	1.1 – 1.5
65	1.0 – 2.0	1.3 – 1.55
89	1.0 – 2.0	1.1 – 1.75
77	4.0 – 5.0	4.1 – 5.0
78	4.0 – 5.0	4.6 – 4.75
88	4.0 – 5.0	4.2 – 4.6
93	4.0 – 5.0	4.5 – 5.07
94	4.0 – 5.0	4.1 – 5.0

TABLE IV

REPRODUCIBILITY OF PROCESS
(TASK II)

Desired Thickness (Mils)	Number of Samples	Size	Mean Thickness of the Batch($\overline{X}$) (Mils)	Maximum Range of Average Sample Thickness (R of $\overline{X}$) (Mils)	Maximum Range of Individual Readings in the Batch (R of X) (Mils)
0.5–1.0	12	3/4" x 3" x .020"	.77	0.6–0.9	0.4–1.1
1.0–2.0	12	3/4" x 3" x .020"	1.46	1.2–2.0	0.9–2.1
	23	3/4" x 7" x .020"	1.54	1.2–1.8	1.0–2.0
4.0–5.0	12	3/4" x 3" x .020"	4.34	4.0–4.6	3.8–5.0

Uniformity

Two factors have been found to greatly affect the uniformity of pyrolytic tungsten deposits; flow distribution as influenced by the sample support system, and the rate of deposition relative to the linear rate of WF_6 flow past the sample. Minimum flow disruption occurs using a support system comparable to that illustrated by Figure 2C thus uniform deposits may be readily produced provided that other processing parameters permit uniform deposition to occur. This leads to the second factor that influences uniformity, WF_6 linear flow rate versus deposition rate. At the higher deposition rates, whether due to increased temperature or increased pressure, the deposit thickness becomes non-uniform; tapering from heaviest at the upstream end to thin at the downstream end. This effect is thought to be due to depletion of WF_6 from the gas stream faster than it is supplied by the linear flow rate down the length of the specimen. At low deposition rates(low pressure and temperature), the reaction rate between hydrogen and WF_6 is relatively slow; thus, depletion of WF_6 from the gas stream as it flows past the sample is relatively low resulting in a more uniform deposit. On the other hand, increasing the velocity of the WF_6 flowing past the sample by increasing the measured WF_6 flow rate, reducing the chamber diameter, or introducing an inert carrier gas as well as using a slight temperature gradient makes it possible to produce uniform deposits at relatively high deposition rates.

Experience has indicated that deposits 4 to 5 mils thick may be produced on 3/4" wide x 3" long tungsten substrates with a total variation in thickness of less than 1 mil at deposition rates up to about 4 mils per hour using hydrogen and WF_6 measured flow rates of 1000 cc/min and 100 cc/min respectively. At rates greater than about 4 mils/hour, increased WF_6 flow is required to maintain the same level of uniformity. Typical variations in the thickness of deposits made at rates less than 4 mils/hour are illustrated by the data previously presented in Table III.

It should be noted that one important ramification of achieving uniform deposits over relatively long lengths, without resorting to complex temperature profiles or moving hot zones, is that the process must be operated non-efficiently. The thickness of the deposit made on any increment of length appears to be directly dependent upon the amount of WF_6 available to it. For maximum uniformity, depletion should be minimized; therefore, efficiency will be low.

In the case of samples heated directly by induction in a cold wall deposition chamber, control of coating uniformity requires that attention be given to the heating profiles and coupling of the sample to the induction heating coil. This is extremely difficult because it involves the shape and thickness of the substrate to be coated, the electrical resistivity and thermal conductivity of the substrate, the integrated change in these properties as pure tungsten is deposited on the substrate, the specific heat and thermal conductivity of both hydrogen and WF_6, and the radiant energy losses from the ends of the sample as well as the lower efficiency of electrical coupling at the end.

The feasibility of using induction as well as radiant sample heating to produce uniform, high quality cladding was established, but considerable effort was expended in both Tasks of of the program on the investigation of these variables and in establishing the technique for

satisfactorily compensating for the many interacting phenomena.

In brief, it may be said that thin, flat W-UO$_2$ plates are more difficult to coat by R.F. induction heating than either thin, flat unfueled tungsten plates or any cylindrical shape. It was also found that as tungsten was deposited on the surface the electrical coupling improved and the sample would heat more efficiently. A reduction in power would compensate for general temperature increases, but if localized hot spots existed it would cause the deposition rate to increase in those areas and further aggravate the non-uniformity.

The effect of deposition gases on uniformity must also be considered. Since the WF$_6$ properties are responsible for rapid cooling at the upstream end of the hot sample, it is necessary to have much tighter coil spacing at the upstream end to make a decreasing thermal gradient on the sample before the WF$_6$ is started and while H$_2$ is flowing. This adjustment is empirical because of the system geometry, but if selected properly it will result in either a uniform temperature along the sample or a slightly increasing temperature gradient downstream after the WF$_6$ flow starts in order to produce uniform coatings. The problem may in part be alleviated by slight preheating of the coating gas or by the use of an induction heated dummy as a preheater. The technique selected must therefore be adjusted to each type of sample to be coated.

Surface Preparation and Crystal Growth

Metallographic examination of deposits made under comparable conditions on recrystallized, unfueled tungsten samples pre-treated in different manners revealed marked differences in both the structure of the deposits and in the degree of interface obliteration. Figure 8 presents a photomicrograph of a deposit made on a substrate that was just degreased with acetone prior to coating. This deposit can be characterized as being columnar in structure with a readily discernible interface between coating and substrate. The structure of this deposit is quite like those made on the walls of the stainless steel plating chamber (see Figure 9 for comparison). This crystalline growth pattern is expected when the tungsten cannot assume the orientation of the crystal lattice of the substrate. Deposits of this nature have been prone to fracture at the interface during sectioning with an abrasive wheel for metallographic preparation.

Figure 10 illustrates the type of deposit produced on a substrate that was etched in 40% HF-60% HNO$_3$ prior to coating. The columnar growth habit and the clearly distinguishable interface indicate that substrate nucleation did not occur. As with the degreased sample, this sample tended to fracture at the interface during sectioning.

A typical deposit made on a sample given the hydrogen reduction treatment(3) prior to deposition is shown in Figure 11. Examination of the structure of the deposit reveals an obvious lack of the columnar structure and a high degree of substrate nucleation and epitaxial growth.
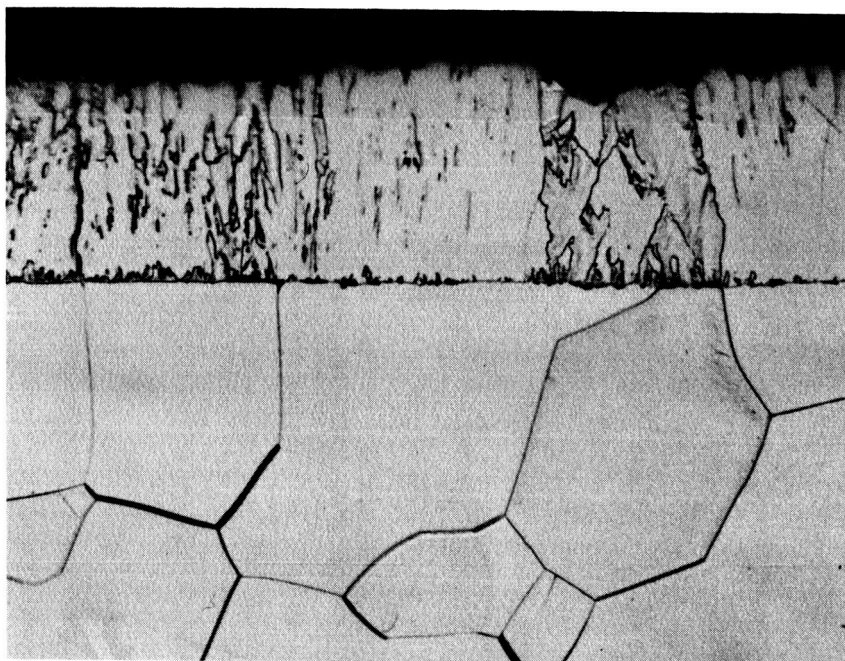
— Cladding

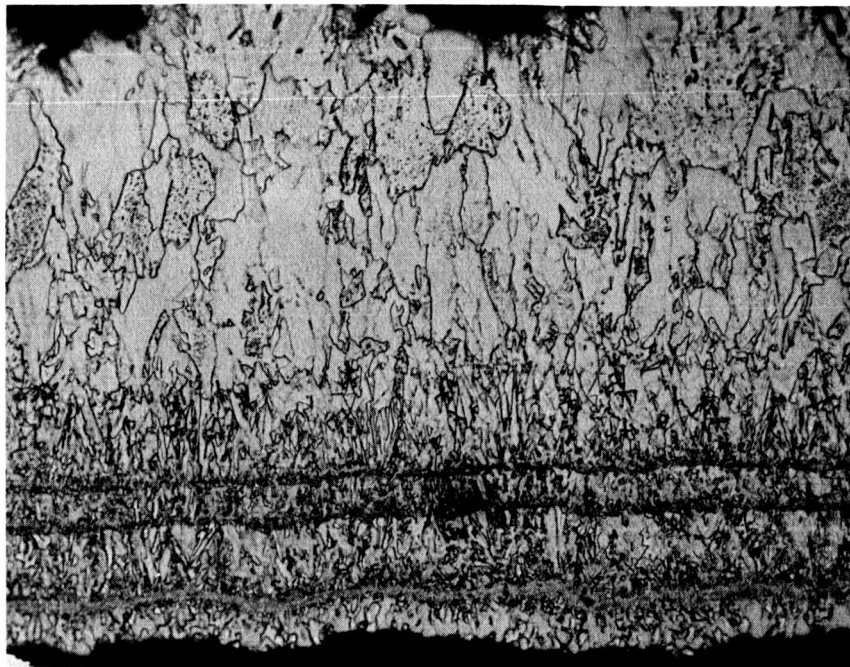— Original Interface

— Substrate

400X   Murakami's Etchant

FIGURE 8

Photomicrograph of a tungsten deposit made on acetone degreased
tungsten substrate. Note columnar structure of deposit and clearly
defined interface. Deposit made at 915°F (490°C), 70 cc/min WF_6,
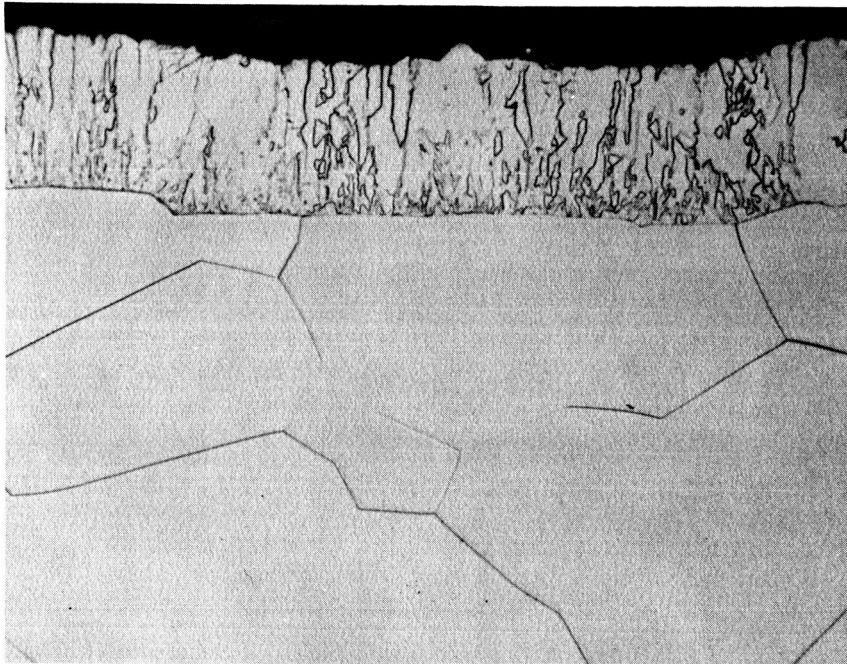4500 cc/min H_2, 38 mm Hg.

250 X   Murakami's Etchant

FIGURE 9

Photomicrograph of a tungsten deposit taken from walls of the
stainless steel plating chamber illustrating natural growth habit
of pyrolytic tungsten.   Bands are the result of a number of
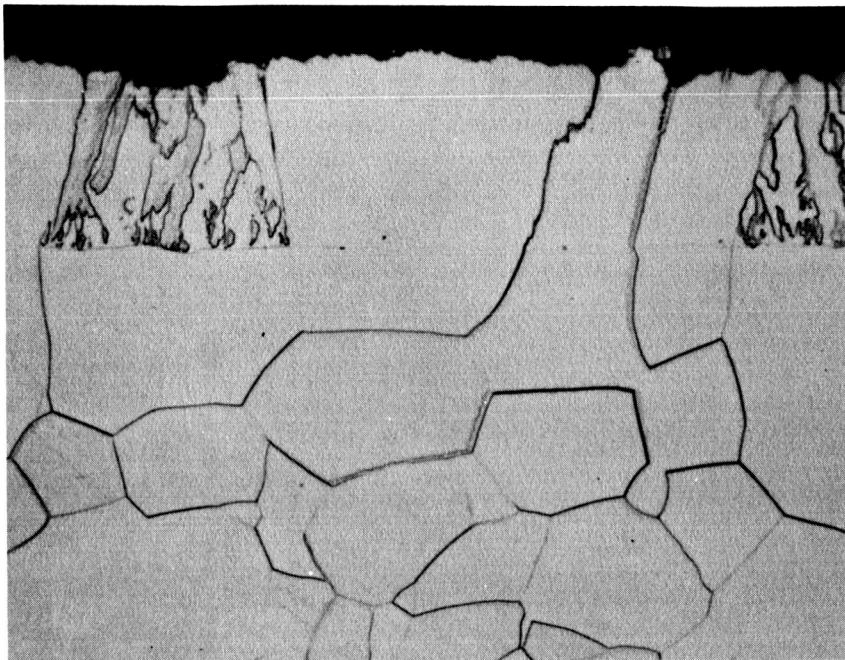deposition runs.

— Cladding

— Interface

—— Substrate

400X   Murakami's Etchant

FIGURE 10

Photomicrograph of a tungsten deposit made on etched (40% HF-
60% HNO$_3$) tungsten substrate. Note columnar growth. Deposit
made at 915°F (490°C) 70 cc/min WF$_6$, 4500 cc/min H$_2$, 42 mm
Hg.

— Cladding

— Interface

— Substrate

400X   Murakami's Etchant

FIGURE 11

Photomicrograph of pyrolytic tungsten deposit made on a tungsten
substrate that was given pre-coating treatment for 5 min. at 1600°F
(870°C) in H_2. Note extensive substrate nucleation and epiaxial
growth with obliteration of the interface. Deposit was made at
915°F (490°C), 70 cc/min WF_6, 4500 cc/min H_2, 36.8 mm Hg.

For the most part, the interface between the deposit and substrate is nearly obliterated. It is postulated, as a result of extensive examination of samples produced in this manner, that epitaxial growth of the deposit occurs on substrate grains whose orientation closely approximates the natural growth orientation of pyrolytic tungsten. On grains whose orientation widely differs from the deposit, epitaxial growth seems to begin but is apparantly superceded by the natural growth habit of the deposit and the columnar structure results. The hydrogen reduction pretreatment provides the requisite clean, oxide-free surface on which substrate nucleation may occur.

As shown in Figure 12, the same high degree of epitaxial growth was observed in deposits made on substrates prepared by etching in 40% HF-60%HNO_3 followed by the hydrogen reduction pre-treatment.

An additional factor that appears to influence the nature of the bond between the deposit and substrate and the degree of epitaxial growth is the ratio of hydrogen flow to WF_6 flow. Metallographic examination of deposits made on etched and hydrogen pretreated substrates at H_2:WF_6 ratios from 10:1 to 150:1 suggests that epitaxial growth is most predominant in deposits made at low ratios and slow rates of growth. Comparison of the photomicrographs presented in Figures 13 and 14 illustrates this effect. Figure 13 shows the microstructure of a deposit made at an H_2:WF_6 ratio of 10:1. A high degree of epitaxial growth and complete elimination of the original interface (approximately 90%) can be readily seen in this photograph. Figure 14, which depicts the structure of a deposit made at 150:1 H_2:WF_6 ratio, shows extensive epitaxial growth but a more readily discernible interface. Specimens coated at intermediate ratios showed intermediate degrees of interface visibility with the trend to being less discernible at lower ratios.

As previously mentioned, the rate at which the deposit is made influences the structure of the deposit to some extent. In a substrate nucleated deposit made at low deposition rates epitaxial growth dominates for the entire thickness of the deposit and flat surfaced grains are formed. In substrate nucleated deposits made at relatively high deposition rates, however, epitaxial growth seems to degenerate into columnar growth after a few mils producing grains with serrated outer surfaces.

From the standpoint of adherence, it is obvious that coatings with a high degree of substrate nucleation will have a higher bonding strength than coatings with non-epitaxial, columnar growth. This point is well illustrated in Figure 15, two photomicrographs of a sample that received rather abusive treatment during sectioning with an abrasive disc. Since cracking occurred in the substrate during sectioning, it is apparent that the strength of the bond between cladding and substrate is at least equal to intergranular bonding strength in most areas.

It has been demonstrated that the 1600°F (870°C) hydrogen pretreatment prior to deposition in either radiant heated or induction heated systems is as effective for promoting excellent bonding and epitaxial growth on W-20 v/o UO_2 composites as it is for unfueled, recrystallized tungsten. Photomicrographs of typical deposits made on NASA supplied W-UO_2 composites pretreated in hydrogen prior to cladding are presented in Figures 16 and 17. As seen in the

Astronuclear
Laboratory
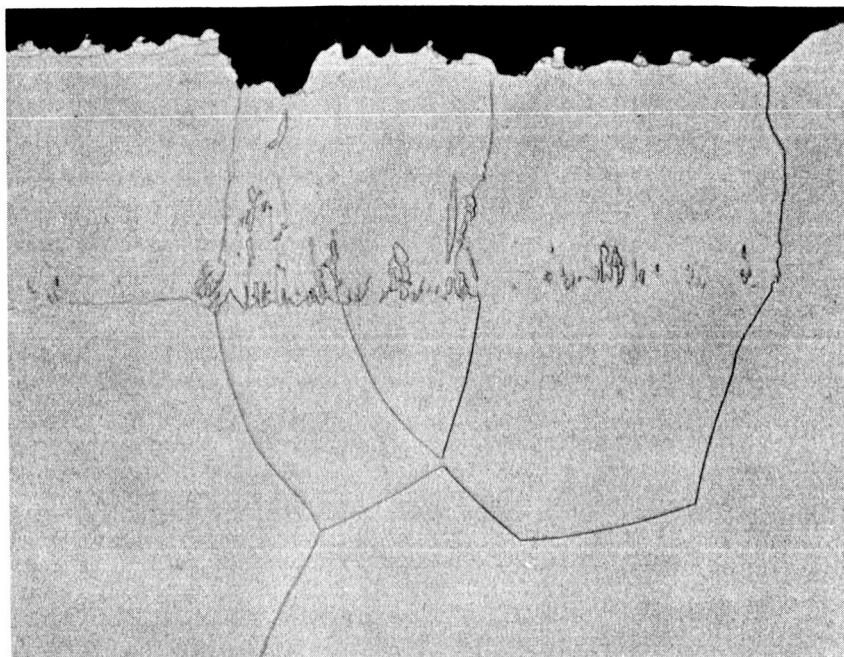
—Cladding

__Interface
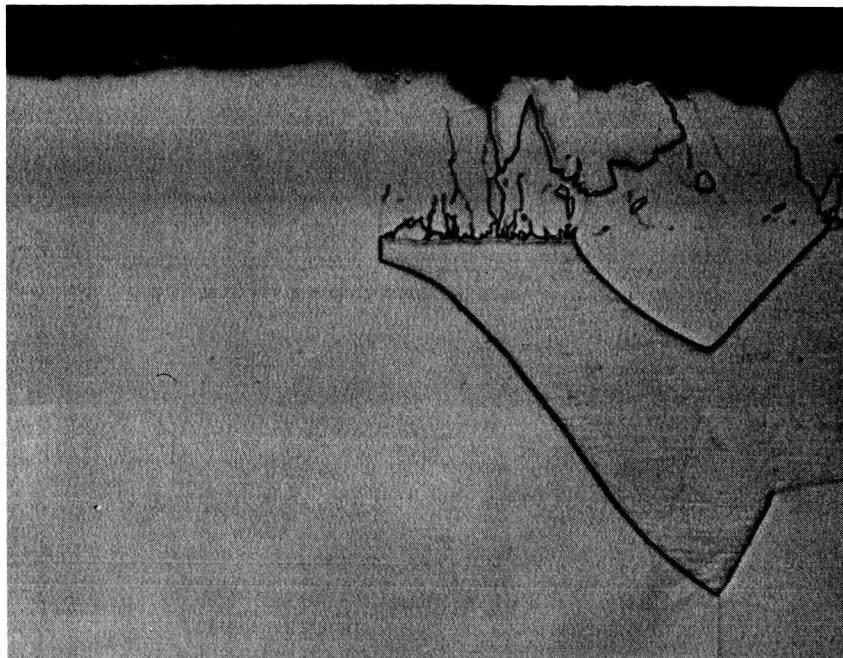
— Substrate

400X   Murakami's Etchant

FIGURE 12

Photomicrograph of a tungsten deposit made on a tungsten substrate
that was etched in 40% HF 60% HNO_3 followed by 5 min. in H_2
at 1500°F (815°C) prior to coating. Deposit was made at 915°F
(490°C), 70 cc/min WF_6 flow, 4500 cc/min H_2, 66 mm Hg.

500X   Murakami's Etchant

FIGURE 13

Tungsten deposit made at H_2:WF_6 ratio of 10:1 on etched and
H_2 pretreated tungsten substrate showing extensive epitaxial
growth and complete obliteration of interface.   Deposition
parameters were 915°F (490°C), WF_6-50 cc/min, H_2-500 cc/min,
pressure - 31 mm Hg.
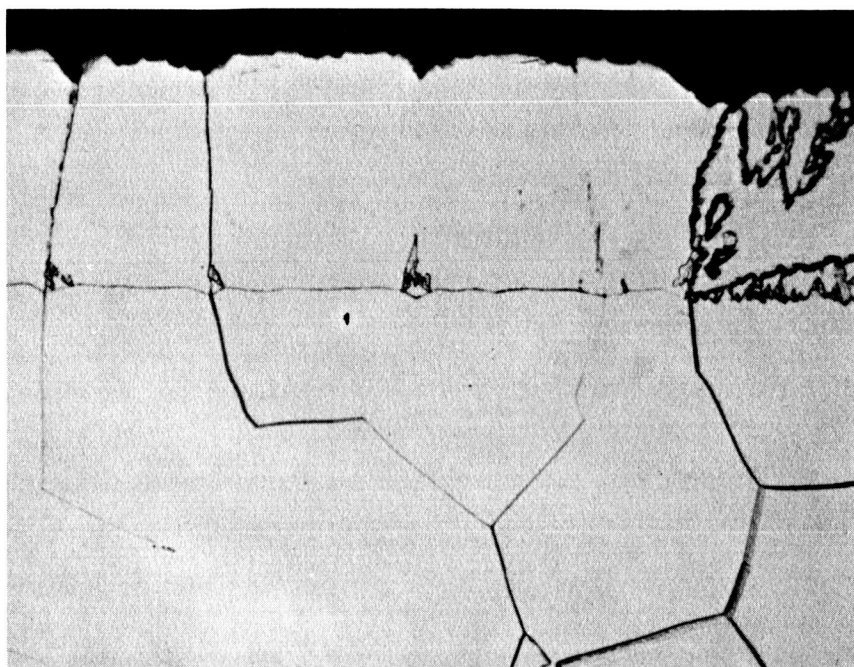
400X   Murakami's Etchant

— Cladding

— Interface

— Substrate

FIGURE 14

Tungsten deposit made at $H_2:WF_6$ ratio of 150:1 on etched and H_2 pretreated tungsten substrate. Note epitaxial growth and presence of definable interface. Deposition parameters: 915°F (490°C), 6000 cc/H_2, 40 cc/min WF_6, 46 mm Hg.
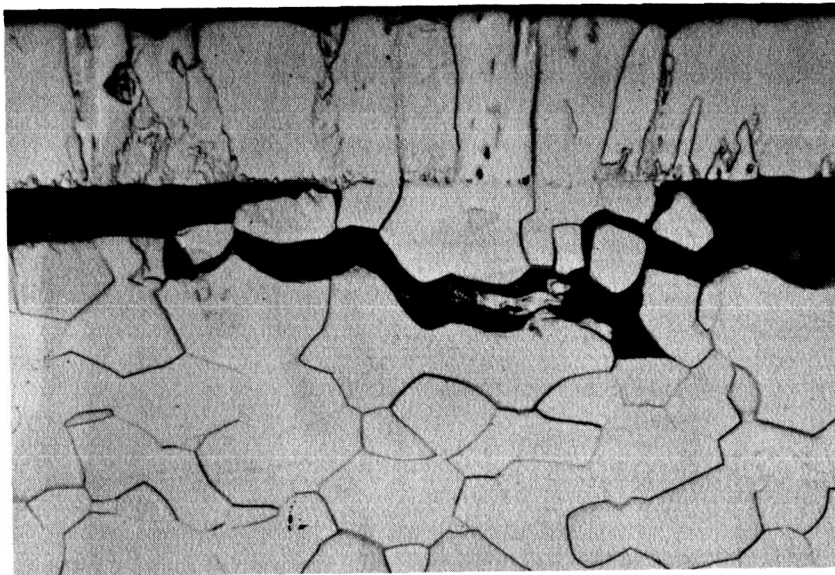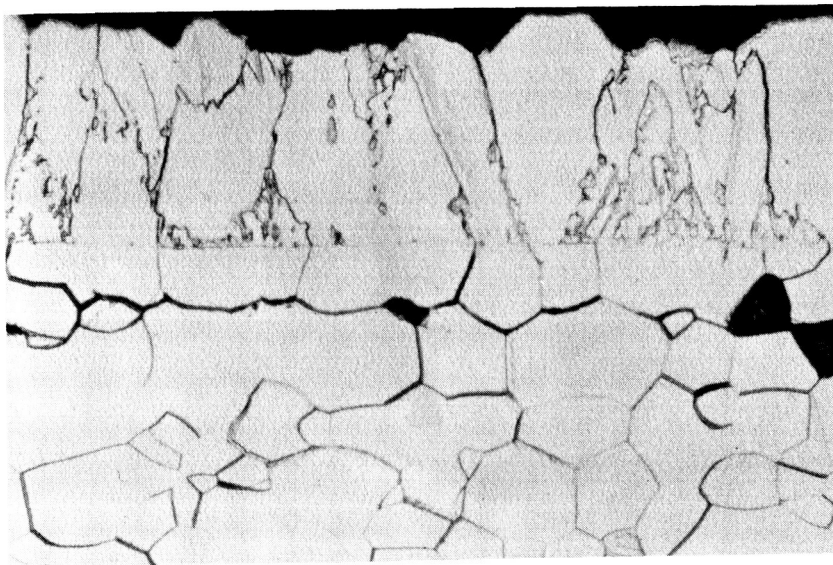
400X   Murakami's Etchant

—Cladding

—Interface

—Substrate

400X   Murakami's Etchant

—Cladding

—Interface
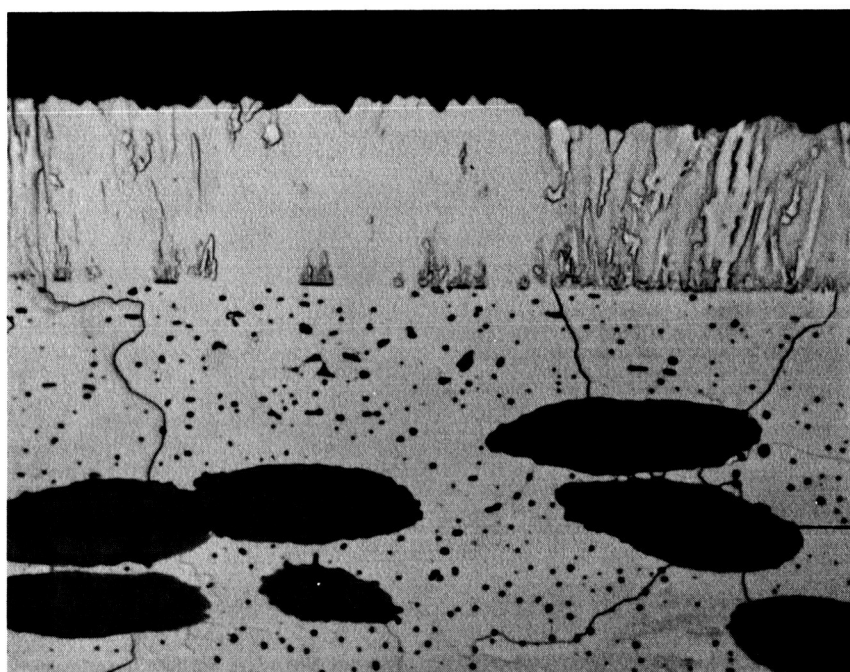
—Substrate

FIGURE 15

Photomicrographs of a longitudinal section through a sample that received
unusually rough treatment during abrasive disc sectioning showing that the
coating bond strength may exceed intergranular strength. This deposit was
made at 915°F (490°C), WF_6 flow 70 cc/min, H_2 flow – 4500 cc/min, at
42 mm Hg pressure on a hydrogen pretreated substrate.

— Cladding

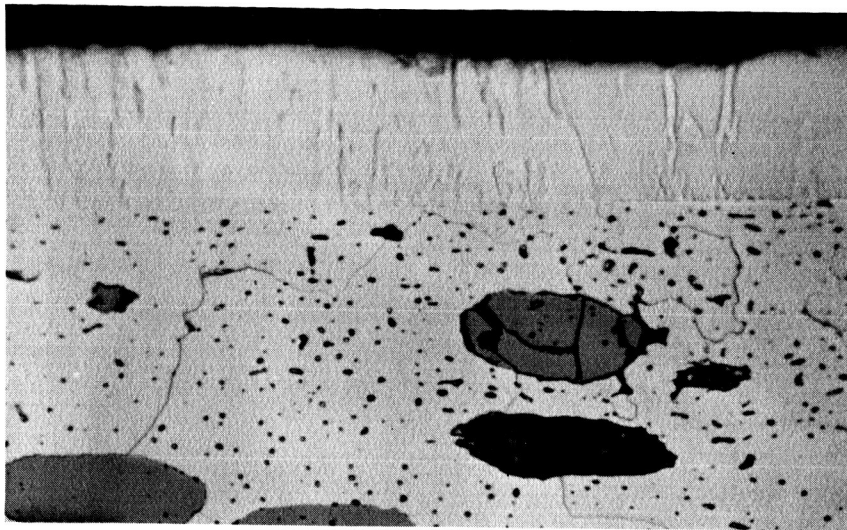— Original Interface

— W Substrate

— UO₂

400X   Murakami's Etchant

FIGURE 16

Photomicrograph of pyrolytic tungsten deposit on W-20 v/o
UO₂ produced in radiant heated system.   Following pre-
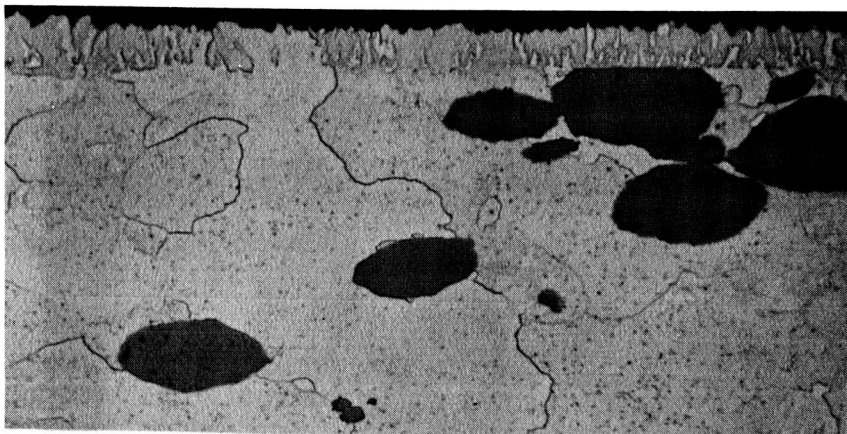treatment in H₂ at 1600°F (870°C) for 15 mins.
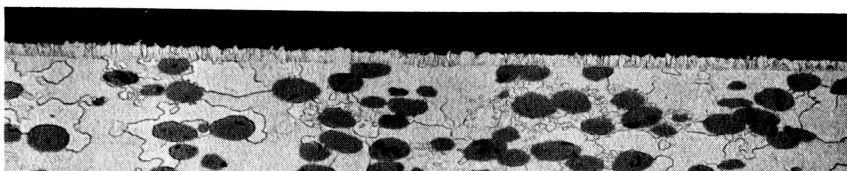
34

400X

— Cladding

— Interface

— Substrate

400X

— Cladding

— Interface

— Substrate

100X   Murakami's Etchant

— Cladding

— Interface

— Substrate

FIGURE 17

Photomicrographs of pyrolytic tungsten deposit on W-20 v/o
UO$_2$ produced in induction heated system following pre-
treatment in H$_2$ at 1600°F (870°C) for 15 minutes.

photomicrographs, the bond between the core and cladding is excellent and a high degree of interface obliteration is evident.   Little difference exists between radiant and induction heated samples. Typically, the structure of deposits made on fueled substrates is about 50% columnar and 50% epitaxial. As predicted by previous experiments, deposits on the composites exhibit a columnar growth habit over UO_2 particles that are exposed at the interface because the crystal structure of the UO_2 is not conducive to substrate nucleation. This effect is illustrated in Figure 18. Figure 18 also provides an example of the throwing power of the process in that it shows that the vapor deposited tungsten penetrates and fills voids and cracks that are exposed to the original compact surface. This is further illustrated by Figure 19, a section through the hole and support wire of a sample coated in the induction heated system. It is readily observed that the deposited tungsten has penetrated into the gap between the hole and wire and completely sealed the support wire into the composite. The implications of this observation to joining and cladding intricate fueled composites are only limited by ones imagination.

Density

Metallographic examination of all deposits made over a wide range of parameters in both systems has indicated that the deposits are free from voids and porosity and approach theoretical density. The density of a 5 to 10 mil thick tungsten deposit produced on a copper mandrel has been determined to be 19.4 g/cm^3. This determination was made by the water displacement method after the copper mandrel had been dissolved. Although the measured value of 19.4 g/cm^3 is greater than the recognized value of 19.3 g/cm^3, it is within the limits of accuracy of the determination and indicates that the density of the deposit closely approached theoretical density. The x-ray density of tungsten deposits has been determined to be 19.245 g/cm^3.

Bend Tests

To demonstrate the adherence of vapor deposited tungsten to plain and fueled tungsten substrates, a series of bend tests were run at temperatures from room temperature to $1000°F$ ($540°C$). In these tests 2" x 3/4" coated samples were heated to the specified temperatures and then bent around a 0.025" radius over a 0.75" span in a tensile testing machine. Both unfueled, recrystallized tungsten and $W-UO_2$ samples coated at temperatures from $660°F$ ($350°C$) to $1295°F$ ($700°C$) were tested. The bend tests included one sample which had been exposed to hydrogen at $4500°F$ ($2480°C$) for 2 hours. All samples were pretreated at $1600°F$ ($870°C$) in hydrogen in the deposition chamber prior to cladding with tungsten. Test results are tabulated in Table A-I.
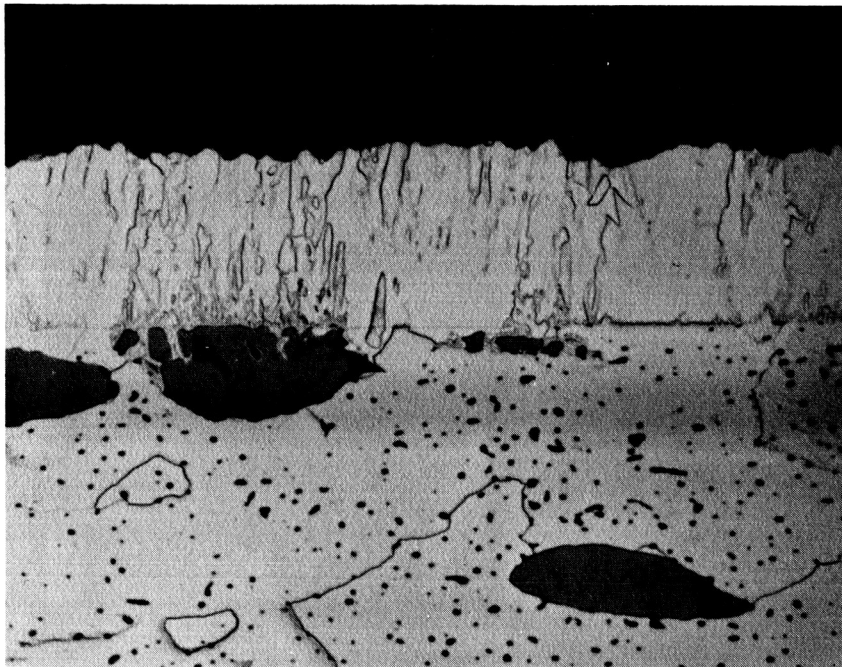
400X   Murakami's Etchant

FIGURE 18

Photomicrograph of pyrolytic tungsten deposit on W-20 v/o
UO_2. Note columnar growth habit of deposit on UO_2 particle
at the interface and penetration of tungsten into voids and
cracks in the UO_2.

Astronuclear
Laboratory
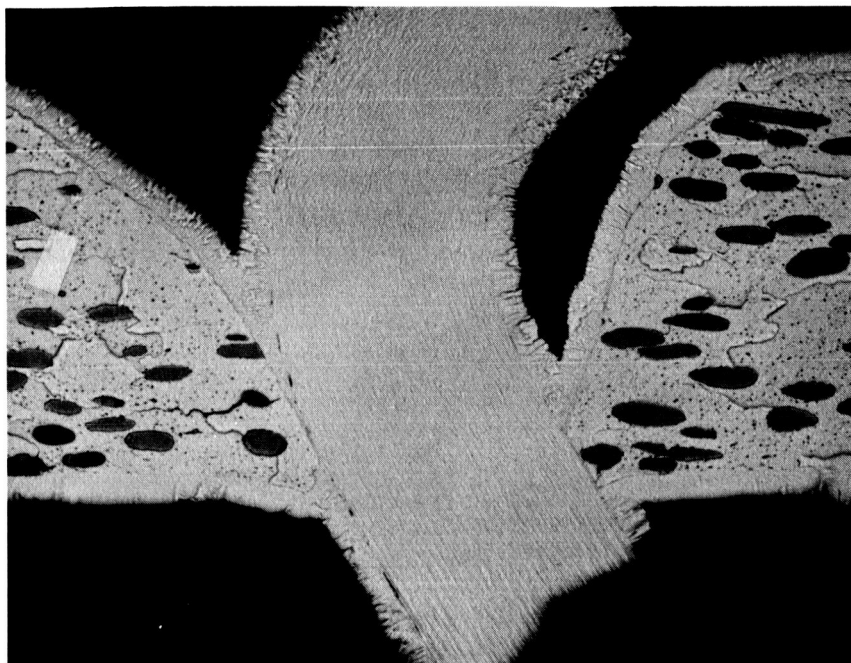
100X   As Polished

FIGURE 19

Section through hole and support wire in W–UO$_2$ sample
coated in the induction heated system.

Metallographic examination of sections through the bend area in each of the samples revealed that in no instance did the coating separate from the substrate during the test. Photomicrographs of typical samples are presented in Figures 20 through 22.

Effect of Post Deposition Heat Treatment on Bond Strength

It has been observed that the quality of the bond between the deposit and substrate and the microstructure of the deposit may be altered by post-deposition heat treatment. Figure 23 illustrates a tungsten deposit made on a degreased substrate. As such, the deposit is columnar in structure with a readily discernible interface. This same deposit, after recrystallization at 3600°F (1980°C) for ten minutes at 10^{-6} mm Hg pressure, is shown in Figure 24. From the photomicrograph, it can be seen that extensive recrystallization has occurred in the deposit and that grain growth has proceeded across the original interface.

Extensive metallographic examination of several unfueled tungsten samples clad under conditions that were not conducive to substrate nucleation and good bonding indicated that they were prone to fracturing at the clad-substrate interface during sectioning with an abrasive cut-off wheel. After heat treatment for 10 minutes at 3600°F (1980°C) in vacuo, sections from the same samples, which then exhibited enhanced bonding, did not fracture at the interface during sectioning.

The effect of post deposition heat treatment on the structure of the cladding after environmental testing will be discussed in the appropriate sections which follow.

Microhardness of Tungsten Deposits

The hardness of tungsten deposits produced under several sets of parameters is presented in Table V. Comparing the deposit hardness values on the basis of temperature one finds that deposit hardness tends to increase slightly with deposition temperature. Examination of the data for the as-deposited versus the post-deposition, heat treated condition of 3600°F (1980°C) for 10 minutes in vacuum reveals that the hardness of the tungsten deposit is reduced by this thermal treatment.

Non-Destructive Testing

A limited non-destructive testing study was conducted to determine whether or not the quality of the bond between clad and substrate could be readily defined. Coated, unfueled, tungsten substrates embodying degrees of clad bonding from non-adherent mechanical bonding produced on an oxidized substrate to tightly adherent epitaxially grown deposits were examined in this study. These samples were evaluated by eddy current techniques and by pulse echo ultrasonic techniques at 5, 19, 15, and 25 mc using a 3/8" diameter crystal with the result that no definable difference was detected between samples over the complete range of bonding. Studies conducted by others[9] indicates comparable difficulty using these techniques.
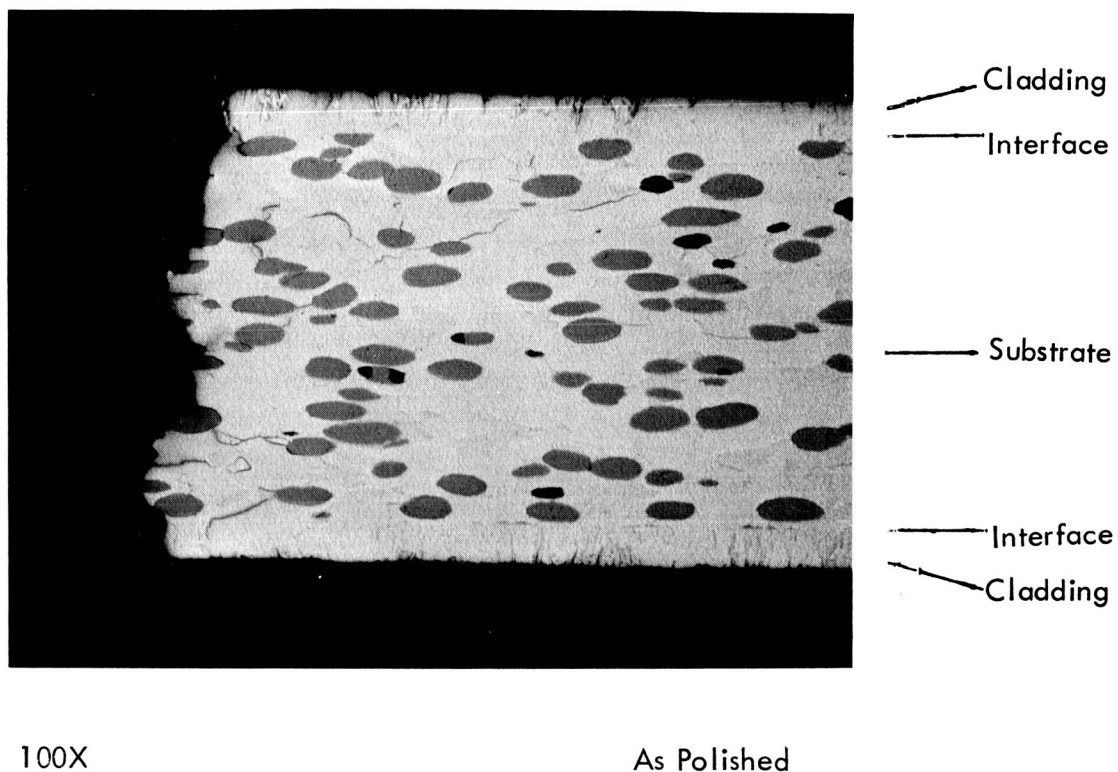
100X   As Polished

FIGURE 20

Tungsten clad W-UO$_2$ composite after bend testing at
room temperature.

W Astronuclear
Laboratory
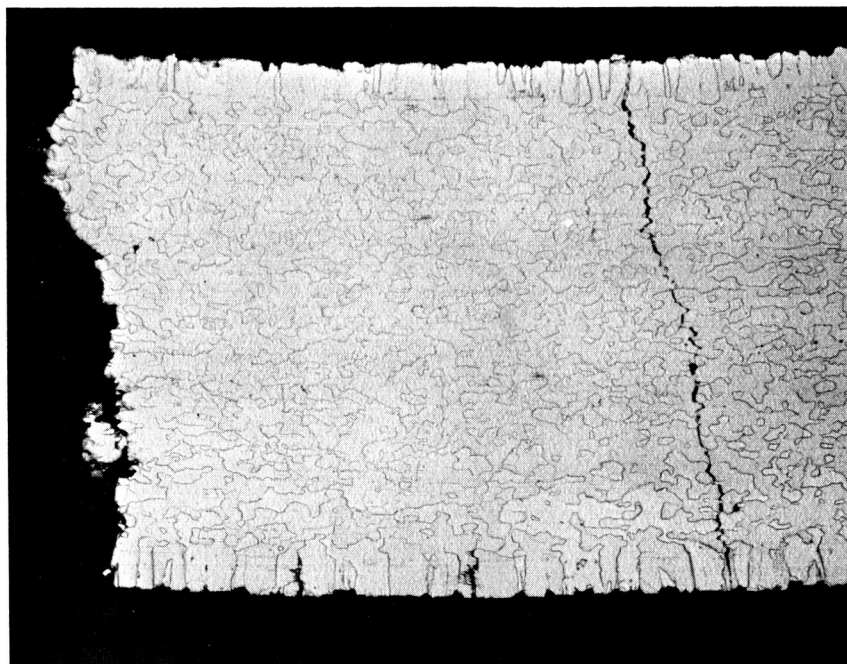
Cladding

Interface

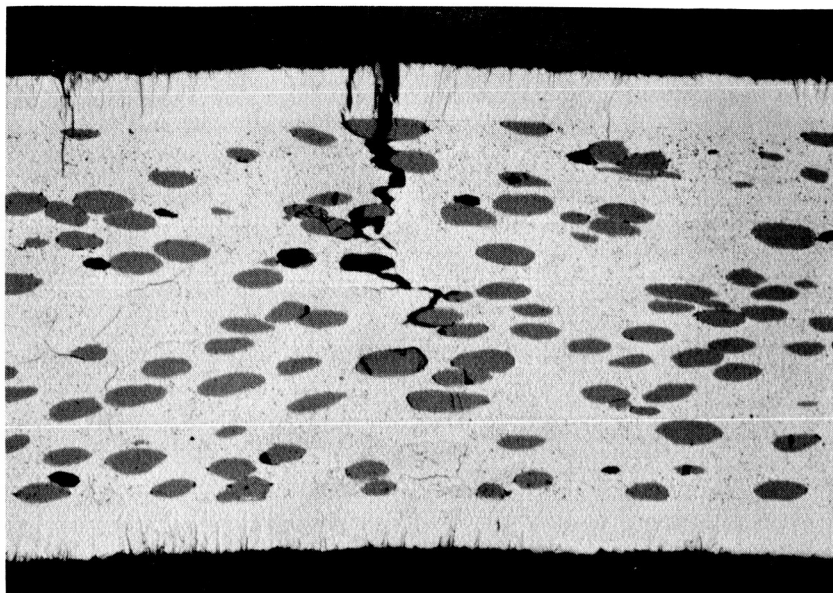Substrate

75X   Murakami's Etchant

FIGURE 21

Tungsten clad plain tungsten after bend testing at
800°F (430°C).

100X   As-deposited   Murakami's Etchant
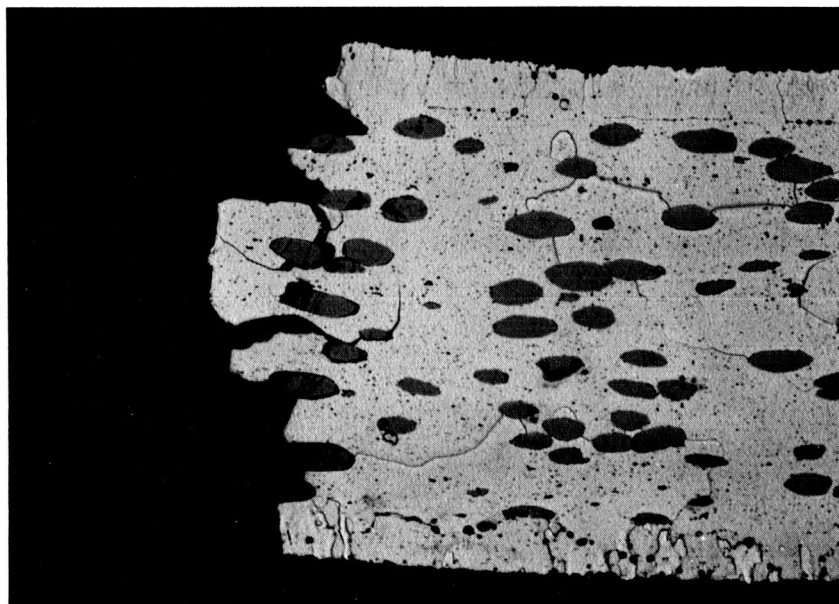
100X   Murakami's Etchant
After testing at 4500°F (2480°C) in hydrogen for 2 hours

FIGURE 22

Tungsten clad W-UO$_2$ after bend testing at 1000°F (550°C)

-- Cladding

--- Interface
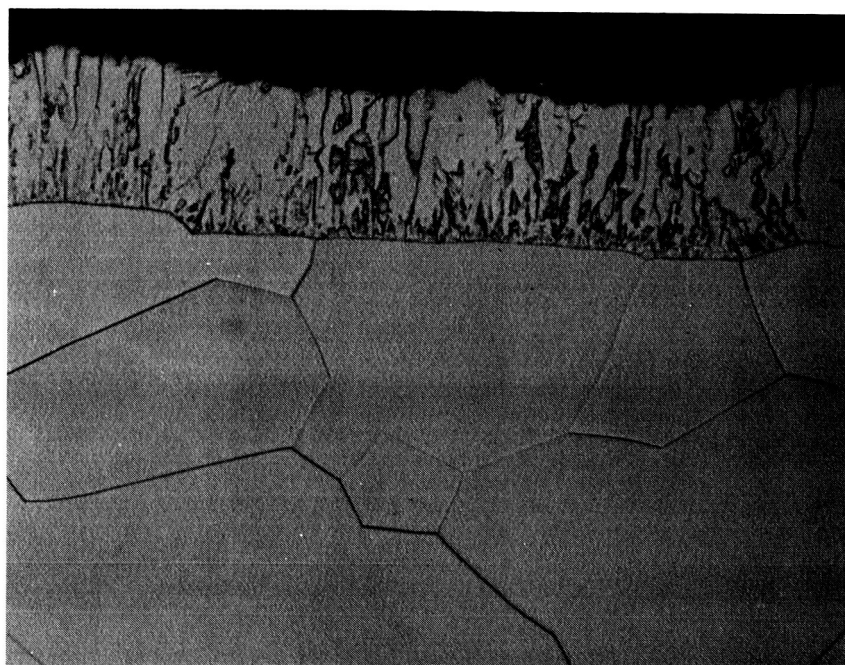
— Substrate

400X   Murakami's Etchant

FIGURE 23

Section of deposit made on an unfueled, recrystallized
tungsten substrate that was just degreased prior to plating.

-Cladding

-Original Interface

-Substrate

400X   Murakami's Etchant

FIGURE 24

Section through same sample shown in Figure 23 after
recrystallization at 3600° F (1980°C) for 10 minutes in vacuo.

Astronuclear Laboratory

TABLE V

MICROHARDNESS OF VAPOR DEPOSITED TUNGSTEN

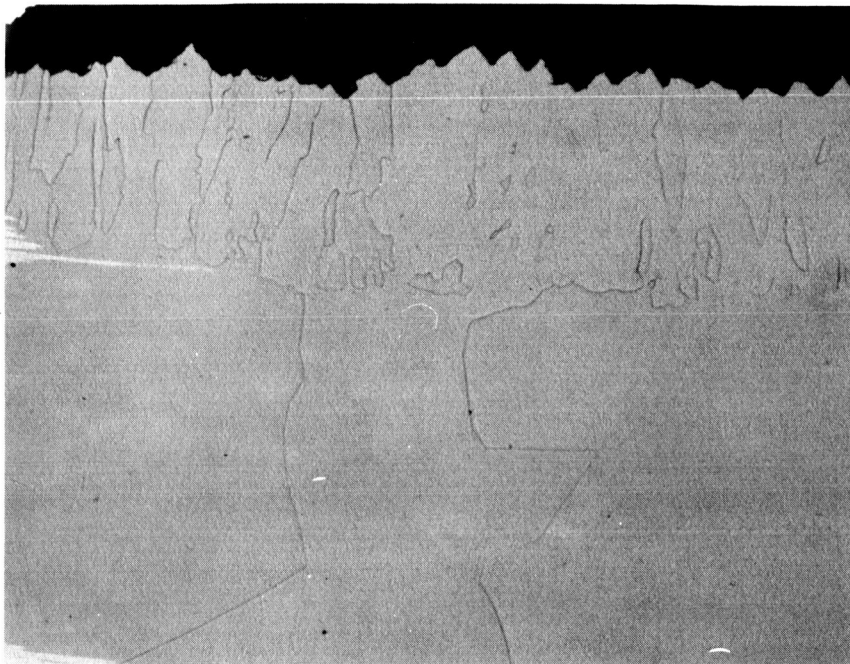| Sample No.	36	35	34	18	24	78	23	Avg.
Depo. Temp. (°C)	360	450	550	490	490	480	490	
Substrate	WK-126	WK-126	WK-126	KD-1169	KD-1169	WK-126	W-UO$_2$	
Microhardness (DPH, 50 Kg load)								
Clad (as deposited)	498,488	597	622,564	645,612	543,780		543,597	595
Core (as deposited)	472,487	498,405	492,472	421,401	433,449		429,342	
Clad (post depo. H.T.)[1]				482,487	425	390,524		465
Core (post depo. H.T.)[1]				449,405	342,390	612,449		

[1] 3600°F (1980°C) for 10 min. at 10^{-6} mm Hg.

Fluorescent penetrant inspection of 0.0005" to 0.005" thick deposits produced on both unfueled, recrystallized tungsten and on W-20 $^v/o$ UO_2 composites has revealed no detectable defects.

Impurity Content

Analytical data on the impurity content of tungsten deposits produced on unfueled, re-crystallized tungsten substrates are presented in Table VI together with an analysis of the substrate material. Analyses for the elements listed were performed using the entire sample, i.e., both substrate and deposit; therefore, to define the concentration of each element in the deposit alone, the reported data had to be proportioned.

Perusal of the table reveals that with the exception of Cu, Si, C, and possibly Ca and F, the concentration of each of the 26 elements sought is less than 10 ppm. The presence of up to 19.8 ppm copper in the deposits may be the result of copper pick-up from the copper tubing used extensively in the deposition system. The silicon determinations listed are seriously questioned due to the wide discrepancy between the values reported by the laboratory and the substrate supplier. The source of carbon concentrations of 22 ppm and 32.5 ppm in the deposits is thought to be oil that back streams from the vacuum pump in the system. Although the cold trap in the system is maintained at about -115°F (-80°C) with dry ice and alcohol to preclude back streaming, two possible factors in favor of back streaming oil contamination may be postulated. First, the trap used might not have been sufficiently efficient to completely eliminate back streaming. Secondly, at this point in the program, the system was evacuated to less than about 25µ prior to filling the cold trap. It is therefore possible that back streaming had already occurred to an extent capable of causing the measured carbon contamination. In addition, a discrepancy also exists between results of the supplier and the analytical laboratory for carbon. It is therefore possible to estimate that both the silicon and carbon content could be less than 10 ppm. Limitations on funding prevented further effort.

It is disconcerting that the limits of detection for the methods used by one analytical laboratory to determine calcium and fluorine levels are 100 ppm and 20 ppm respectively. Review of the system components and source materials, however, indicates that calcium con-centrations in the deposit should be rather low since no sources of this element can be conceived. (Analytical results at NASA on similar specimens indicated calcium to be approximately 3-5 ppm.) With regard to fluorine, it may just be said, at this juncture, that the concentration of fluorine in pyrolytic tungsten deposits made on unfueled, recrystallized tungsten is less than 20 ppm as determined in one laboratory.

Due to the possibility of a reaction between fluorides in the gas stream and UO_2 exposed to the surface of W-UO_2 compacts during vapor deposition of the cladding, additional work on fluorine contamination was performed in this area at a second analytical laboratory. Fluorine concentrations for two W-20$^v/o$ UO_2 samples, one clad at 985°F (480°C), the other clad at

Astronuclear
Laboratory

TABLE VI

IMPURITY CONTENT OF VAPOR DEPOSITED TUNGSTEN

Concentration (ppm)

Sample	WK-126	WK-126-47	WK-126-51
Deposit to Substrate Wt. Ratio	As-Received	2.5/1	5.5/1
Element			
Al	5	3	3
Mg	120	7	2
Cu	5	11.5	19.8
Fe	34	4	3
Ni	5	4	3
Si	>150 (1)*	37	37
Be	< 5	5	< 5
B	< 5	5	< 5
Na	3.95	0.9	6
Ca	<100	<100	<100
Ti	< 5	< 5	< 5
V	< 5	< 5	< 5
Cr	< 5	< 5	< 5
Mn	< 5	< 5	< 5
K	0.81	0.47	2.6
Zr	< 5	< 5	< 5
Mo	< 10	< 10	< 10
Cd	< 5	< 5	< 5
Sn	< 5	< 5	< 5
Pb	< 5	< 5	< 5
N_2	< 5	1	13
O_2	9	4.4	4.6
C	81 (22)*	22	32.5
Co	< 1	< 1	< 1
S	8	8	8
F	< 20	< 20	< 20

*Values reported by the vendor are substantially lower indicating the amount reported in the deposit may be much lower.

$1295^\circ F$ ($700^\circ C$), are presented in Table VII along with fluorine assays for the as-received W-UO$_2$ compacts. These data may be interpreted in two ways. First, it may be assumed that the fluorine is combined with uranium at the clad-core interface in the form of UF$_4$. If this is the case, the similar total fluorine concentrations of 2.8 and 3.0 suggest that fluorine pick-up at both temperatures is equal since the starting samples were of equal area. On the other hand, if it is assumed that the fluorine is uniformly distributed throughout the deposits, the fluorine concentrations in the $895^\circ F$ ($480^\circ C$) deposit, as proportioned on the basis of clad-to-substrate weight ratios, greatly exceeds that found in the $1295^\circ F$ ($700^\circ C$) deposit; i.e., 75.5 ppm and 15.2 ppm respectively. With this limited information, it was assumed that fluorine distributed throughout the cladding was probably in the form of WF$_4$ or WF$_5$ rather than UF$_4$.

Fuel Retention Testing

In the interest of providing a concise and complete presentation, it is in order at this point to discuss the reasoning that led to the selection of samples for high temperature fuel retention testing in Task I. A summary of the relationship of parameters to desirable cladding qualities is tabulated in Table VIII. In reviewing this table, it is readily seen that a high degree of consistency exists amongst the parameters for satisfying the listed requirements. If the factors that favor precluding a reaction between UO$_2$ and HF are excluded, it is seen that low H$_2$/WF$_6$ ratio, low temperature, low pressure, and pretreatment at $1600^\circ F$ in H$_2$ will yield deposits that will probably meet the remainder of the requirements. High H$_2$/WF$_6$ ratio, high temperature (in excess of $1295^\circ F$ ($700^\circ C$)) and removal of the UO$_2$ from the surface of the compact by acid etching or vacuum extraction are factors which inhibit fluorination of UO$_2$ particles exposed to the surface of W-UO$_2$ compacts. It was with this information in mind that the fuel retention test samples were clad with pyrolytic tungsten and subsequently tested at $4500^\circ F$ ($2480^\circ C$) in flowing hydrogen for 2 hours.

Results of these tests are presented in Table IX. Weight losses from the clad compacts resulting from exposure to hydrogen at $4500^\circ F$ ($2480^\circ C$) were extremely low; so low that the weight changes noted bordered on the lower limit of sensitivity of the balance. Analysis of these data as a function of deposition parameters reveals that the measured weight losses are all of the same order of magnitude regardless of the conditions at which the cladding was deposited. Furthermore, the predicted beneficial effects of post deposition heat treatment and removal of surface UO$_2$ are not reflected in these data.

Metallographic examination of samples after the fuel retention test has proven to be significantly more definitive than weight loss data for revealing subtle differences in the behavior of deposits produced at various parameters. Figure 25 is a photomicrograph of a longitudinal section of W-20 v/o UO$_2$ with as deposited tungsten cladding applied at $895^\circ F$ ($480^\circ C$), 10:1 H$_2$/WF$_6$ ratio. Figure 26 is a similar sample, No. 56 with clad deposited at the same conditions, after testing for 2 hours at $4500^\circ F$ ($2480^\circ C$) in flowing hydrogen. Of

Astronuclear
Laboratory

TABLE VII

FLUORINE CONCENTRATION IN W-20% UO_2 COMPACTS
CLAD WITH TUNGSTEN BY VAPOR DEPOSITION FROM WF_6

| | | | F Concentration (ppm) | |
Sample	Cladding Temp.	Wt. Ratio - Clad to Substrate	Total Sample	Clad Only as Extrapolated on Basis of Wt. Ratio
53	700°C	1.55/7.87	3.0	15.2
54	480°C	.25/6.73	2.8	75.5
1	Not Clad	--	<1	--
2	Not Clad	--	<1	--

TABLE VIII

Factors Favoring Meeting Cladding Requirements

Requirement	Deposition Parameters Favoring Meeting Requirements				Other
	H_2/WF_6 Ratio	Temperature (°C)	Pressure (mm Hg)	Pretreatment	
Good Bonding	Low	Low	Low (< 20 mm)	15 mins. in H_2 at 1600°F	Favored by slow growth rate
High Density	Probably optional	Low	Low	Optional	Favored by slow growth rate
Uniformity	(Ratio of WF_6 flow rate to deposition rate - parameters can be arranged.)				
Structure of Coating — epitaxial	Low	Low	Low	15 mins. in H_2 at 1600°F	Favored by slow growth rate
— columnar	High	High	High	Degrease only	Not consistent with good bonding (1)
No fluorination of UO_2	High	≈700	Low	Optional	Removal of surface UO_2 by acids or vacuum extraction.
Impurity Level	Probably optional	Optional	Low	Optional	Gas purity, system cleanliness, system leak tightness.
Freedom from cracks	(Consistant with good bonding and relative coefficients of thermal expansion of substrate and cladding.)				

(1) It might be possible to produce adherent columnar deposits by beginning deposition using parameters that favor good bonding then change to parameters favoring rapid growth.

Astronuclear Laboratory

TABLE IX

Results of Fuel Retention Testing of W-UO$_2$ Clad with Vapor Deposited Tungsten

| Sample No.	Ratio	Deposition Temperature (°C)	Coating Parameters(1) Pressure (mmHg)	Post Deposition Heat Treatment(2) Yes	Post Deposition Heat Treatment(2) No	Coating Thickness (mils)	Wt. Loss after 2 Hrs. at 4500°F in H$_2$ mg/cm^2	Wt. Loss after 2 Hrs. at 4500°F in H$_2$ % of Contained UO$_2$	Remarks
56	10/1	480	17		X	2.4	.069	.11	
56-1	10/1	480	17	X		2.4	.077	.12	
71	10/1	480	17		X	1.3	.131	.21	UO$_2$ removed from surface with HNO$_3$
72	10/1	480	17	X		1.5	.119	.19	UO$_2$ removed from surface with HNO$_3$
57	8/1	700	17		X	2.3	.082	.13	700° deposit less than 1 mil thick
	10/1	480	17						
55	8/1	700	17		X	3.0	.057	.10	700° deposit less than 1 mil thick
	10/1	480	17						
57-1	8/1	700	17	X		2.9	.074	.12	700° deposit less than 1 mil thick
	10/1	480	17						
59	10/1	480	17		X	3.6	.086	.15	.003 abraded from one side prior to cladding to remove Zr contaminated layer.

(1) All samples were pretreated at 1600°F (870°C) in H$_2$ for 15 mins. prior to cladding.

(2) 3600°F (1980°C) at 10^{-6} mm Hg for 15 mins.
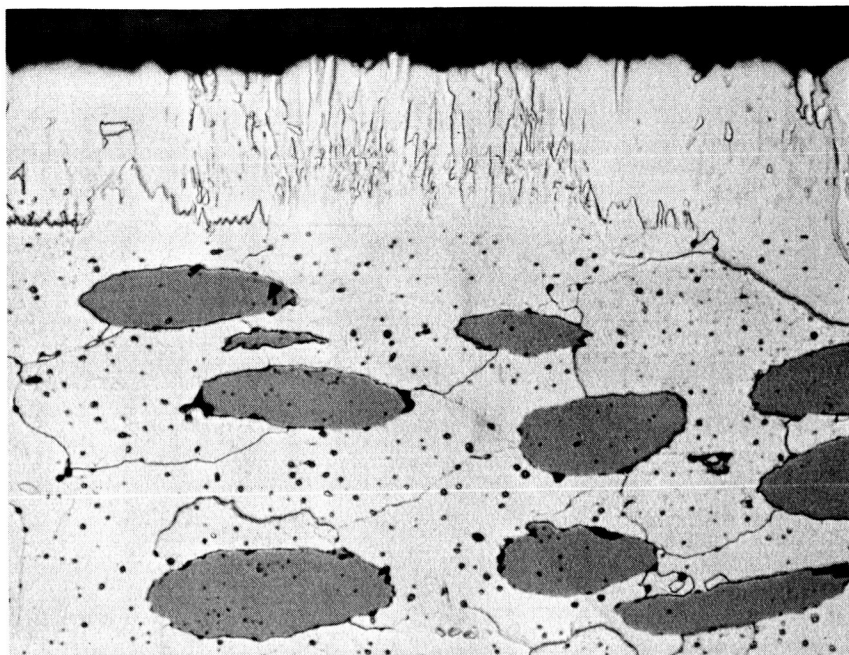
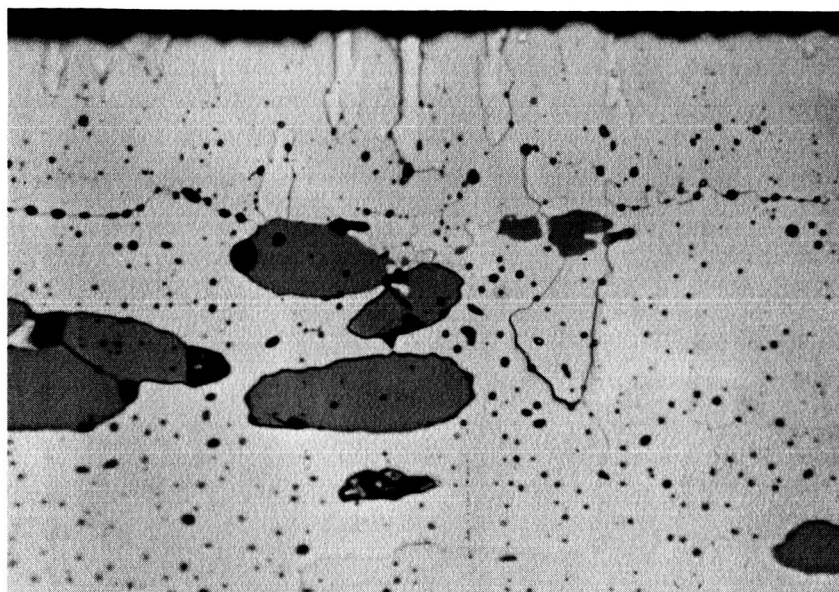400X   Murakami's Etchant
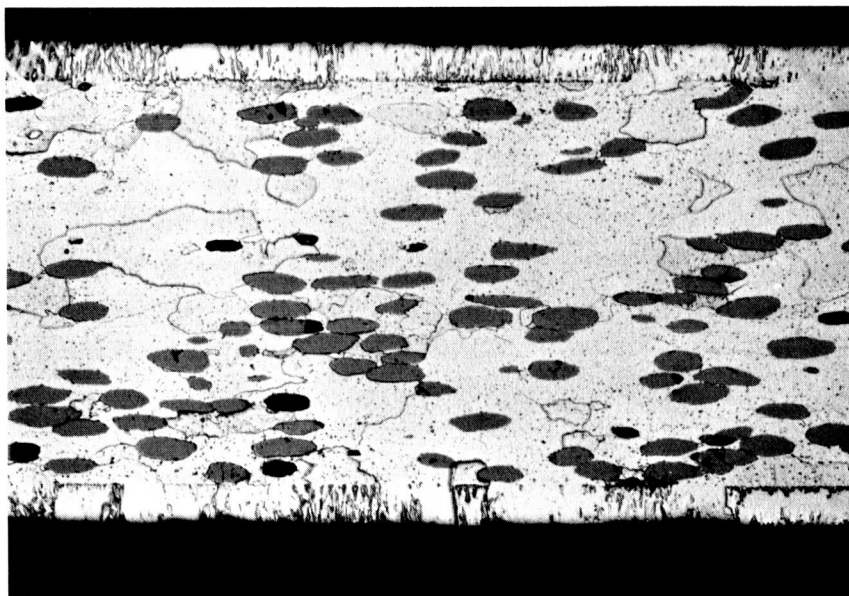
100X   Murakami's Etchant

FIGURE 25

Vapor deposited tungsten on W–20 v/o UO_2 compact. As deposited.
Deposition parameters: 895°F (480°C), H_2/WF_6 – 10/1, 17 mm Hg.
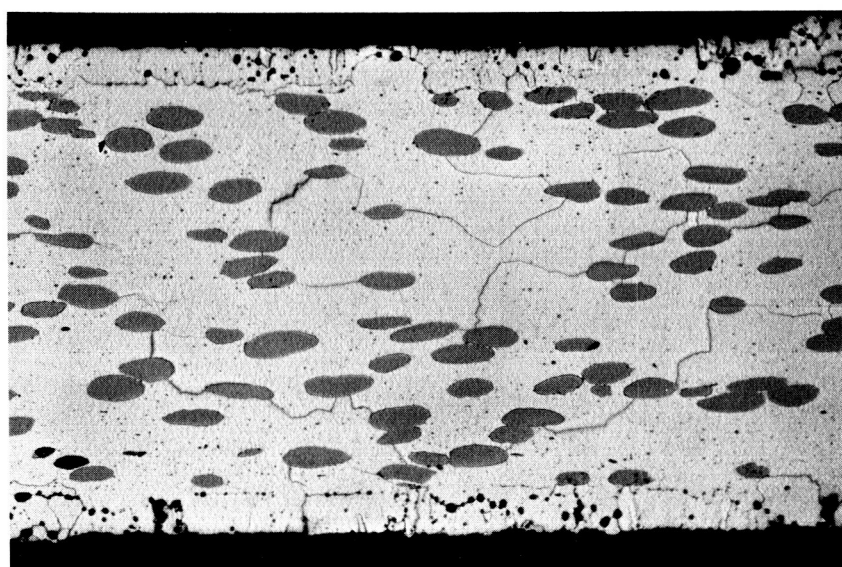Pretreatment: 15 mins. at 1600°F (870°C) in H_2.

Astronuclear
Laboratory

400X   Murakami's Etchant

100X   Murakami's Etchant

FIGURE 26

Sample No. 56 after test at 4500°F (2480°C) in hydrogen for 2 hours.
Deposition parameters: 89.5°F (480°C), H_2/WF_6-10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2.

53

specific interest in this photo is the porosity present in the clad after the test. Attention is called to the apparent densification of the UO_2 during the test and the grain growth usually observed within the tungsten matrix of the composite. These three effects were common to all of the clad composites tested. Fuel densification and grain growth with the $W-UO_2$ compacts remained relatively constant from sample to sample indicating that these resulted solely from the thermal effects (i.e., the cladding conditions had no effect). Porosity formation in the cladding, as will be subsequently shown, exhibited a consistent dependency on deposition parameters, post deposition thermal treatment, and $W-UO_2$ composite batch.

Comparison of the photomicrographs in Figure 27 (Sample 56-1) with those shown in Figure 26 illustrates the effect of post deposition heat treatment on the formation of porosity in the cladding. These samples were cut from the same sheet of $W-UO_2$ stock and clad in the same deposition run. Sample No. 56-1 (Figure 27) was heat treated at 3600°F (1980°C) for 15 minutes in vacuo prior to fuel retention testing. Sample No. 56 (Figure 26) was tested as clad. It is quite obvious that porosity formation is substantially reduced by the post deposition heat treatment.

The cladding on the sample shown in Figure 28 was deposited at two temperatures. In the interest of precluding a reaction between surface exposed UO_2 in the $W-UO_2$ compact and the coating gases, a thin layer of tungsten (less than 1 mil thick) was first deposited at 1295°F (700°C). The sample was then cooled to 895°F (480°C) and the remainder of the cladding (about 2 mils) deposited at this temperature at a more readily controlled rate. Porosity formation in the cladding of this sample after exposure to hydrogen at 4500°F (2480°C) is again apparent. It is interesting to note, however, that the porosity is restricted to the thicker tungsten layer deposited at 895°F (480°C). Little porosity exists in the initial thin layer deposited at 1295°F (700°C) on the $W-UO_2$ surface. The effects of post deposition heat treatment, 15 minutes at 3600°F in vacuo, on the fuel retention behavior of deposits produced at these conditions is illustrated in Figure 29. As seen previously, less porosity is observed in the clad of the heat treated sample after fuel retention testing than after testing the as deposited sample. Again, little porosity is evident in the clad layer that was deposited at 1295°F (700°C) adjacent to the $W-UO_2$ compact surface.

Figures 30 and 31 are photomicrographs of sections through fuel retention tested samples that had the surface exposed UO_2 removed from the $W-UO_2$ composite by etching for 30 minutes in HNO_3 prior to cladding at 895°F (480°C), 10:1 H_2/WF_6 ratio. The sample shown in Figure 30 was tested in H_2 at 4500°F (2480°C) in the as-clad condition. The sample shown in Figure 31 was heat treated at 3600°F (1980°C) for 15 minutes at 10^{-6} mm Hg prior to testing. Review of the two figures reveals that exposure to the fuel retention test environment has produced less porosity in the cladding of both samples than other deposits produced at 895°F (480°C), but again, post deposition heat treatment was most effective.

As previously discussed, trace quantities of zirconium were found in the surface layers of some $W-20 v/o UO_2$ plates. To define the influence of this impurity, a sample which had 0.003" of material removed from one side by abrading was clad at 895°F (480°C), 10:1 H_2/WF_6 ratio and subsequently tested at 4500°F (2480°C) in flowing hydrogen for 2 hours. Photomicrographs of this sample after testing, Figure 32, indicate that essentially no difference exists
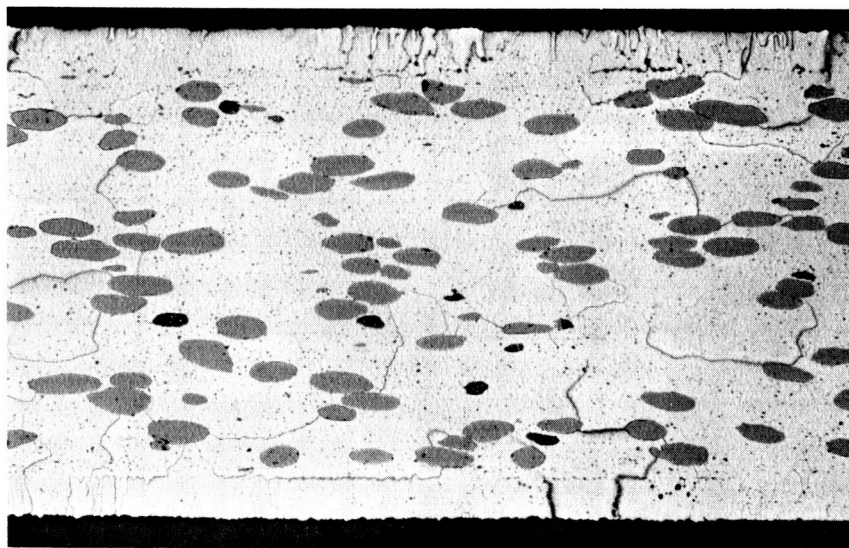
—Cladding
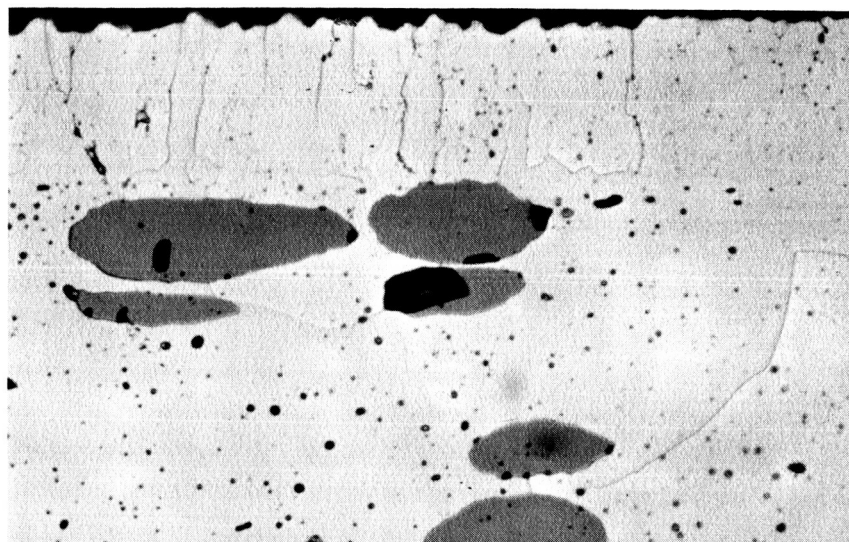
— Original Interface

— Substrate

400X   Murakami's Etchant

— Cladding
— Original Interface

— Substrate

— Original Interface
— Cladding

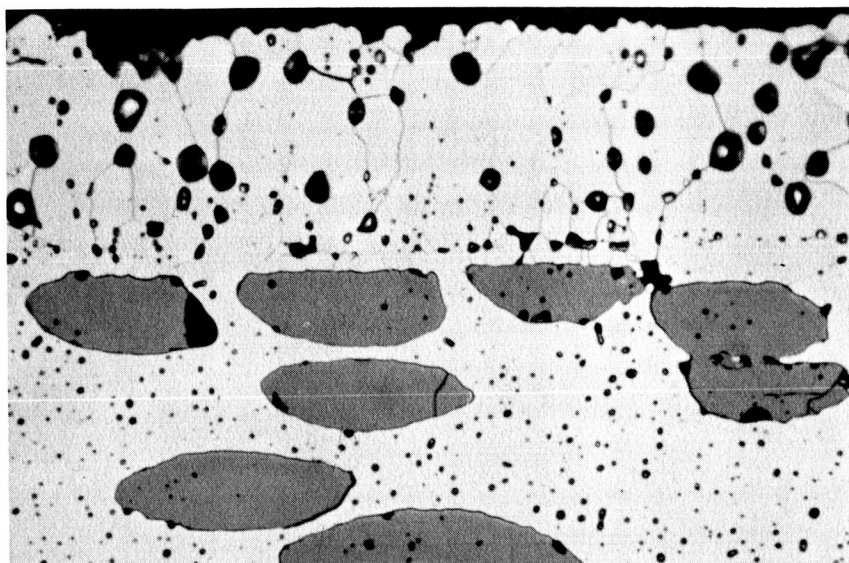100X   Murakami's Etchant

FIGURE 27

Sample No. 56-1 after test at 4500°F (2480°C) in hydrogen for 2 hours
which followed post-deposition heat treatment at 3600°F (1980°C) for
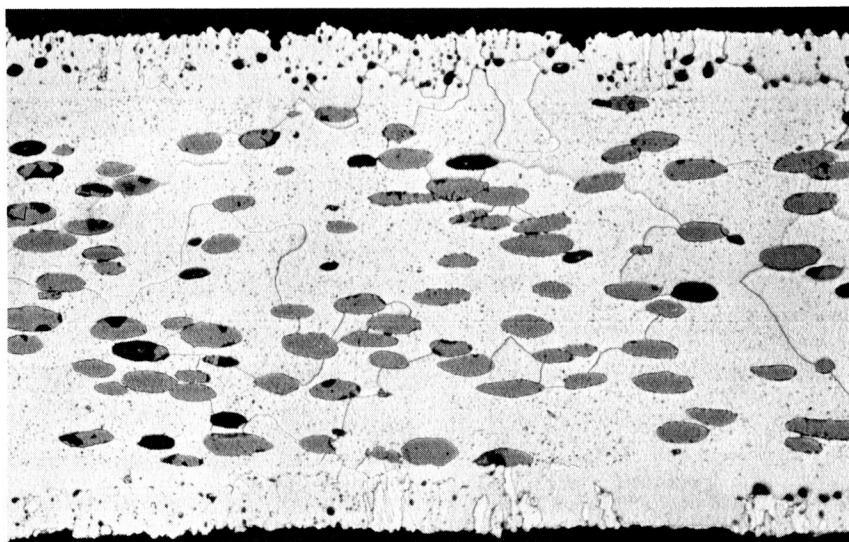15 mins. at 10^{-6} mm Hg.
Deposition parameters: 895° F(480°C), H$_2$/WF$_6$-10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H$_2$.

w Astronuclear
Laboratory

400X   Murakami's Etchant

100X   Murakami's Etchant

FIGURE 28

Sample No. 55 after test at $4500^{\circ}F$ ($2480^{\circ}C$) in hydrogen for 2 hours.
Deposition parameters: $1295^{\circ}F$ ($700^{\circ}C$), H_2/WF_6 -10/1, 17 mm Hg
followed by $895^{\circ}F$ ($480^{\circ}C$), H_2/WF_6 -10/1, 17 mm Hg.
Pretreatment: 15 mins. at $1600^{\circ}F$ ($870^{\circ}C$) in H_2.

—Cladding (480°C)

—Cladding (700°C)

—Original Interface

—Substrate

400X   Murakami's Etchant

—Cladding (480°C)

—Cladding (700°C)

Original Interface

—Substrate

100X   Murakami's Etchant

FIGURE 29

Sample No. 57-1 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
Sample was heat treated (after deposition) at 3600°F (1980°C) for 15 mins.
   at 10^{-6} mm Hg prior to testing.
Deposition parameters: 1295°F (700°C), H_2/WF_6-10/1, 17 mm Hg
   followed by   895°F (480°C), H_2/WF_6-10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2.
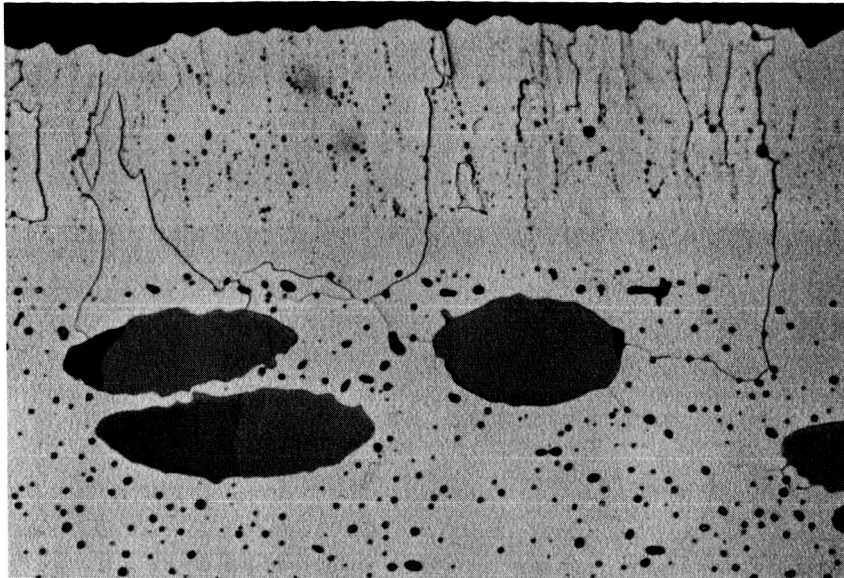
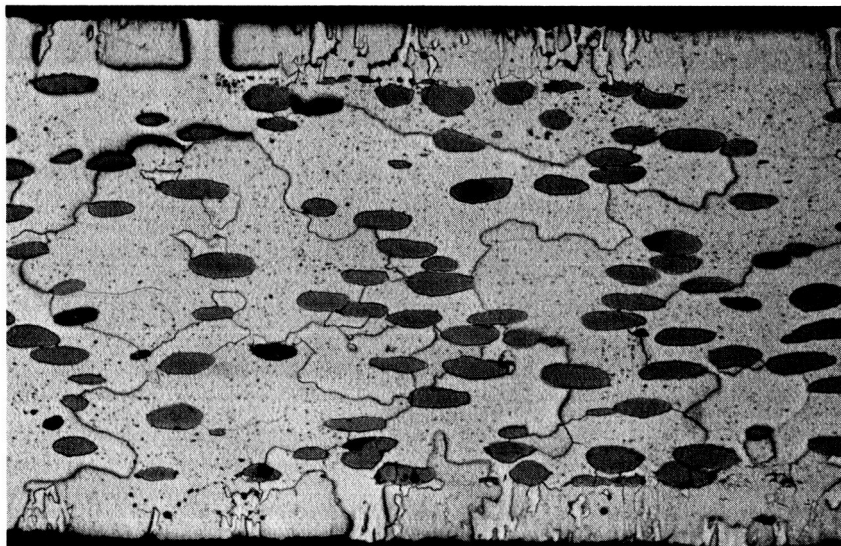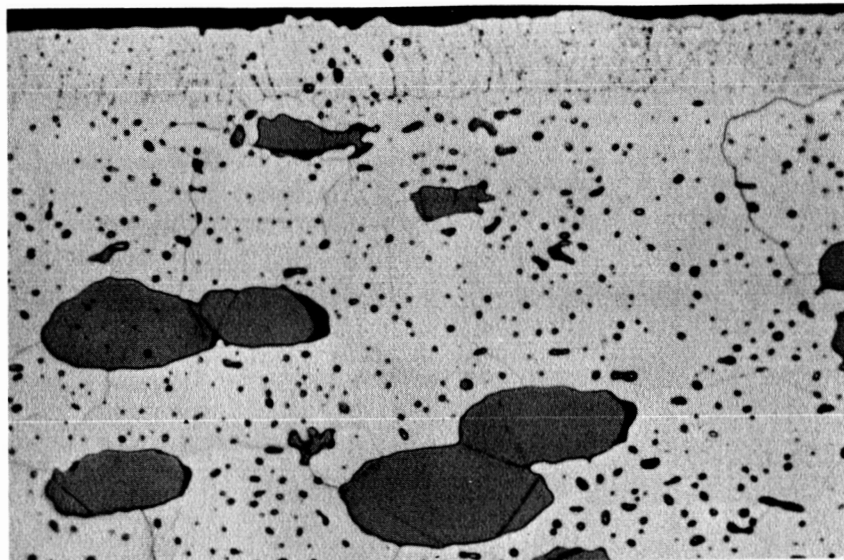400X   Murakami's Etchant

— Cladding
— Original Interface

— Substrate

Cladding
— Original Interface

— Substrate

— Original Interface
Cladding

100X   Murakami's Etchant

FIGURE 30

Sample No. 71 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
UO_2 removed from surface of compact by etching in HNO_3 for 30 mins.
 prior to cladding.
Deposition parameters: 895°F (480°C), H_2/WF_6-10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2.
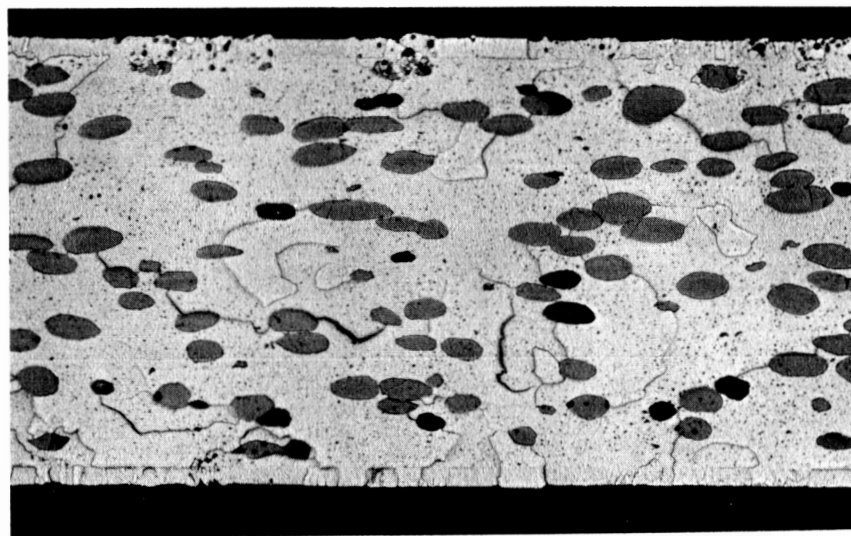
— Cladding
— Original Interface

— Substrate

400X   Murakami's Etchant
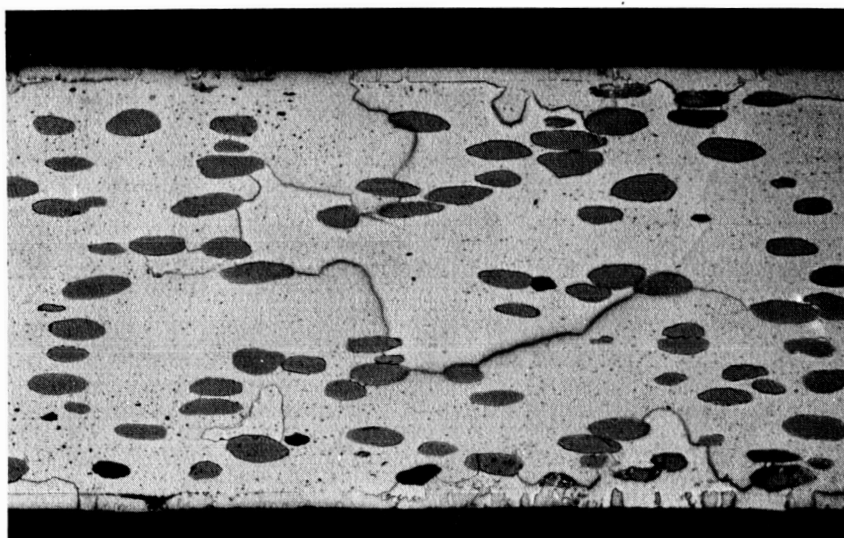
Cladding
— Original Interface

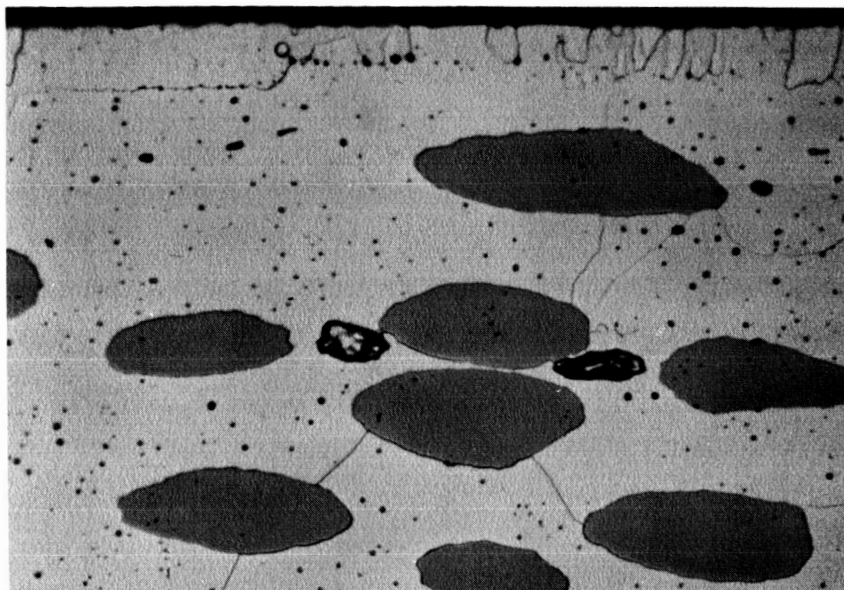— Substrate

— Original Interface
Cladding

100X   Murakami's Etchant

FIGURE 31

Sample No. 72 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
UO_2 was removed from compact by etching in HNO_3 prior to cladding.
Clad compact was heat treated at 3600°F (1980°C) for 15 mins. at 10^{-6} mm Hg
  prior to testing.
Deposition parameters: 895°F (480°C), H_2/WF_6-10/1, 17 mm Hg.
Pretreatment: 15 mins. at 1600°F (870°C) in H_2.

400X   Murakami's Etchant
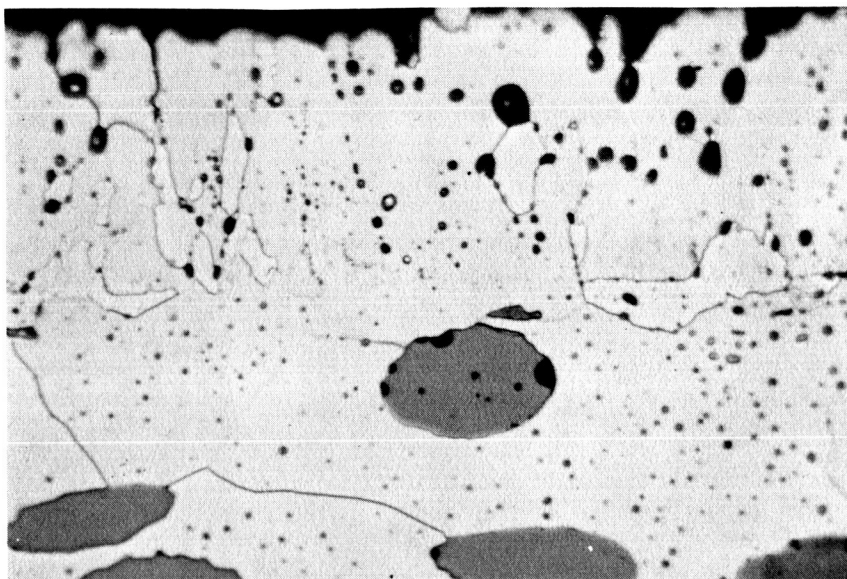
—Cladding

—Original Abraded
   Interface

—Substrate

100X   Murakami's Etchant

—Cladding
—Original Interface

—Substrate

—Original Interface
   Abraded before
   Cladding.

FIGURE 32

Sample No. 59 after testing at 4500°F (2480°C) in hydrogen for 2 hours.
About 0.003" was abraded from one surface prior to cladding.
Deposition parameters: 895°F (480°C), H_2/WF_6-10/1, 17 mm Hg.
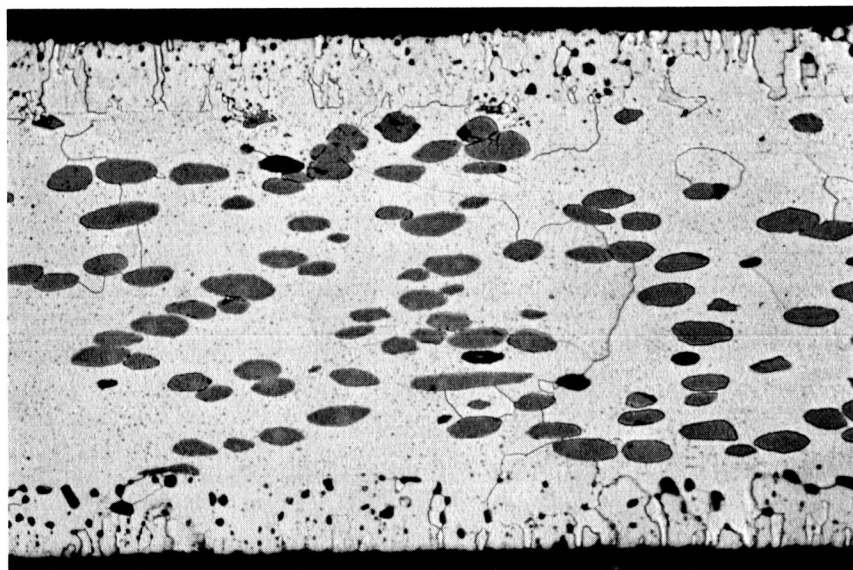Pretreatment: 15 mins. at 1600°F (870°C) in H_2.

in fuel retention behavior between the two sides. More pores formed at elevated temperature on the abraded side. There was no evidence, however, to indicate whether the difference was due to zirconium traces on one side or to the larger surface area exposed on UO_2 particles during the abrasion.

It has been observed that, although weight losses are comparable, larger pores are formed during fuel retention testing in tungsten claddings deposited on $W-UO_2$ composites received from NASA in Batch 2 than are formed in the clad on composites received in Batch 1. This effect, which has been found in samples clad at 895°F (480°C), is illustrated in Figures 33 and 34. Figure 33 is a clad Batch 2 compact after fuel retention testing. Figure 34 is a Batch 1 compact clad and tested under identical conditions. It is evident that the porosity in the cladding on the Batch 2 compact is larger than the porosity seen in the Batch 1 compact. No explanation for this occurrence can be proffered at this time. It is curious to note that the as-received surface of the Batch 1 compacts was markedly discolored, as discussed previously, and that the UO_2 lattice was decidely constricted whereas, the Batch 2 compacts were bright and clean with only slight UO_2 lattice constriction. As a first analysis, one would expect that the above porosity situation would be reversed, i.e., the Batch 2 compacts would behave better than the Batch 1 compacts.

Testing of tungsten cladding on unfueled, recrystallized tungsten substrates at the fuel retention test conditions was done to check on the formation of porosity in the clad. This indicated that porosity formation was apparently a property of the cladding per se (perhaps WF_4 or WF_5), with only little effect being precipitated by the $W-UO_2$ composite during the test or during cladding. A photomicrograph of such a clad, unfueled tungsten sample after testing is shown in Figure 35. Porosity formation is quite similar to that observed in high-temperature-tested, clad, fueled substrates. It was also observed that considerable variation of pore size occurred on the same sample which seemed related to the grain size of the substrate even if not represented in the limited areas of the photomicrographs shown. It was, therefore, apparent that variation of equipment, coating parameters, and the purity of the gases and substrates may all have interrelated effects which were not yet adequately delineated.

From the weight loss data, it was evident that the formation of porosity in the vapor deposited tungsten cladding on $W-UO_2$ composites during single cycle fuel retention testing in Task I did not degrade the effectiveness of the cladding for precluding gross fuel losses. When multiple cycle tests are considered, however, it was conceivable that this porosity might seriously compromise the fuel retention capability of the cladding.

As a result of the work in Task I, it was deemed necessary to continue the investigation of the effect of process parameters and post deposition annealing time on the formation of pores in the vapor deposited cladding prior to the production of test samples. To prevent the needless use of $W-UO_2$ substrates, free standing layers of vapor deposited tungsten were produced at temperatures from 895°F (480°C) to 1290°F (700°C). Sections of these deposited layers were annealed for one hour at 3600°F (1980°C) and 10^{-6} mm Hg. Samples representative of both the as deposited and annealed condition were then tested at 4500°F (2480°C) in hydrogen for two hours, in an environment similar to the high temperature fuel retention test.
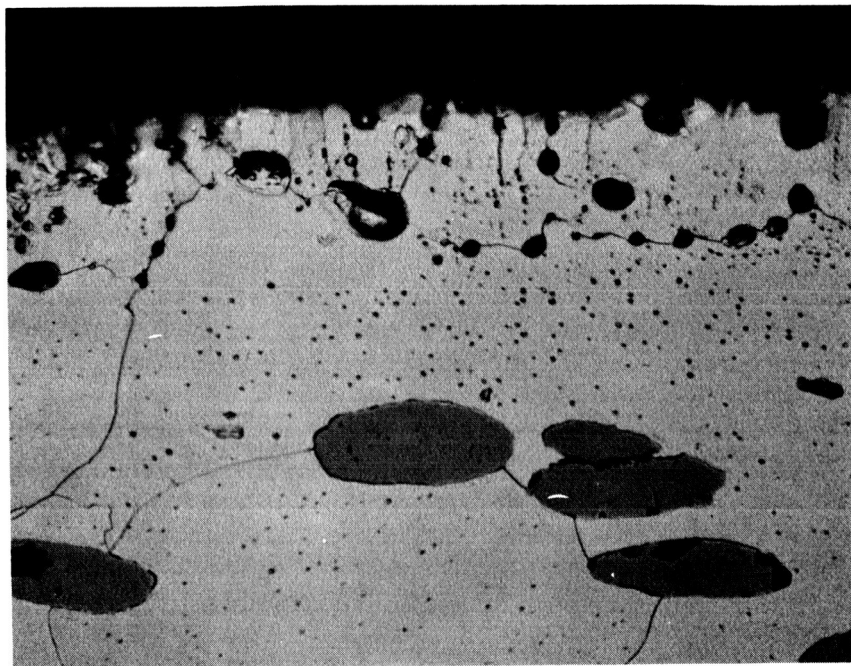
400X   Murakami's Etchant

FIGURE 33

Cladding on NASA W-UO$_2$ compact from Batch 2 after
fuel retention testing.

Deposition parameters: 895°F (480°C), H$_2$/WF$_6$-10/1,
  17 mm Hg.
Pretreatment: 15 mins. at 1600°F(870°C) in H$_2$.
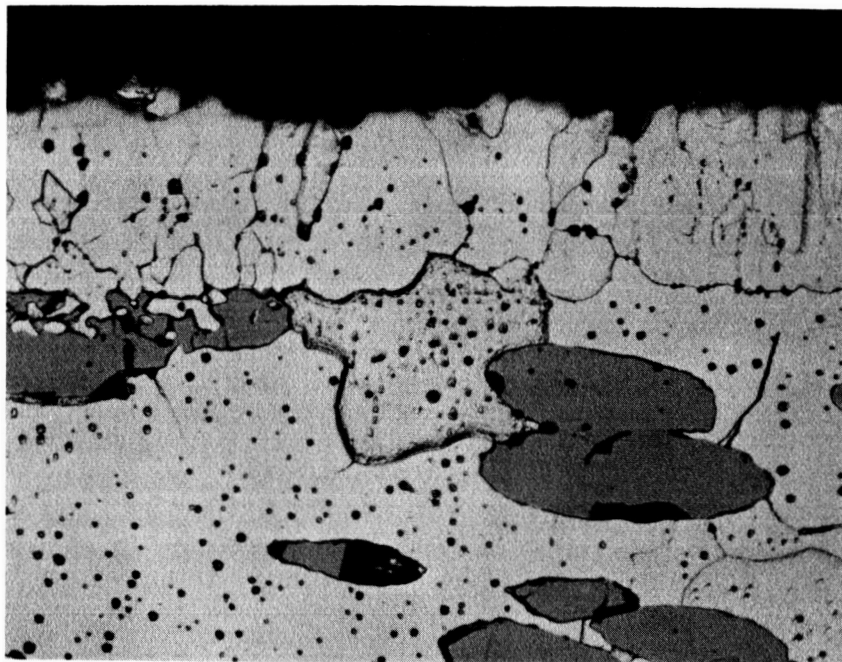
—Cladding

—Original Interface

—Substrate

400X   Murakami's Etchant

FIGURE 34

Cladding on NASA W–UO_2 compact from Batch 1 after fuel
retention testing
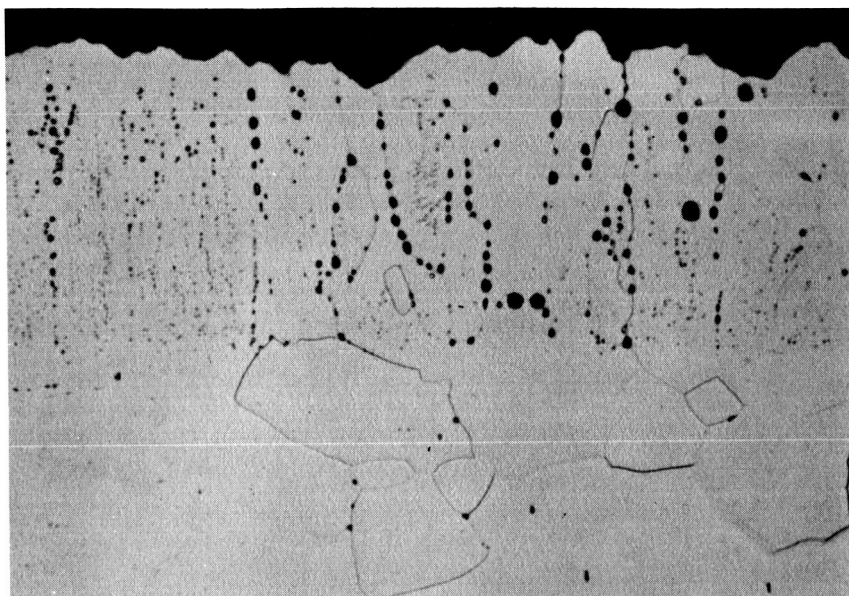
Deposition parameters: 895°F (480°C), H_2/WF_6-10/1,
17 mm Hg.

63
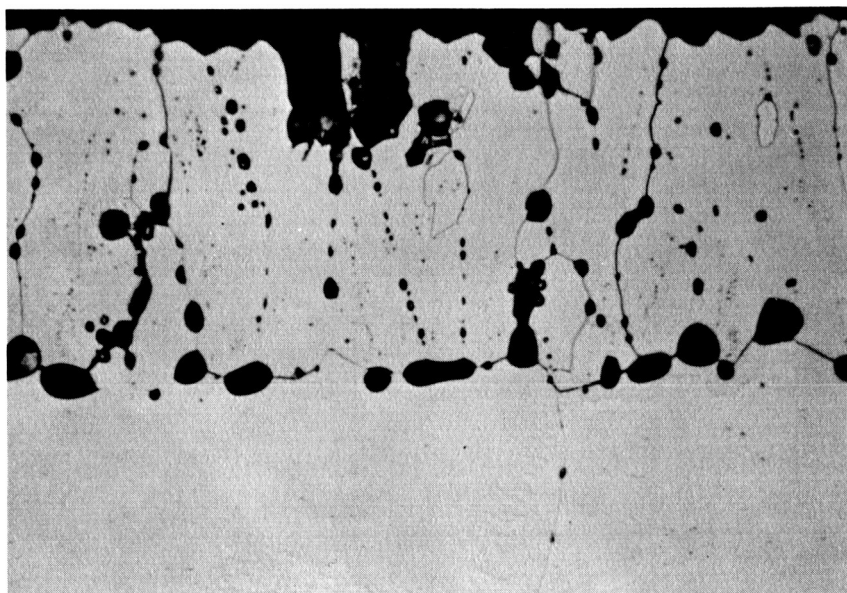
400X   Murakami's Etchant

400X   Murakami's Etchant

FIGURE 35

Two views of tungsten cladding on a sample of unfueled, recrystal-
lized tungsten after testing at 4500°F (2480°C) in hydrogen for
2 hours. Deposition parameters and pretreatment: same as
Figure 33.

The results of these tests are illustrated by the photomicrographs in Figure 36, 37 and 38. Figure 36 shows that the deposition pressure had no effect on the pore formation at 4500°F (2480°C). These results were comparable to those observed in Task I. However, increasing the post deposition annealing time at 3600°F (1980°C) from 15 minutes (which indicated some benefit in Task I) to one hour had a significant effect on reducing the pores formed at 4500°F (2480°C).

Figure 37 shows that cladding deposited at 1150°F (620°C) prevented loss of UO_2, retained high integrity, good bonding, and did not form pores during testing at 4500°F (2480°C) in hydrogen for two hours. It was apparent that the mechanism responsible for the pores was precluded by cladding at that temperature and that no post deposition annealing would be required. Figure 38 shows that a further increase in deposition temperature created a new mechanism which could not be improved by the post deposition annealing. It is not clear at this time whether these pores were caused by growth voids or other impurities entrapped by the higher deposition temperature.

At the conclusion of these experiments, cladding of thirty-six 1/32" x 3/4" x 3" $W-UO_2$ plates, twenty-three 7" x 0.75" x 0.020" $W-UO_2$ tensile specimens, and five cylinders consisting of three unfueled tungsten and two $W-UO_2$ cylinders (0.5" I.D., 0.54" O.D. x 1" long) was initiated. The three inch plates and the tensile specimens were equally divided into types A, B, and C. Coating thicknesses of 0.5 - 1.0 inch, 1-2 mils and 4-5 mils were applied to an equal number of each type of specimen. Tables A-II and A-III lists the specimens and cladding conditions.
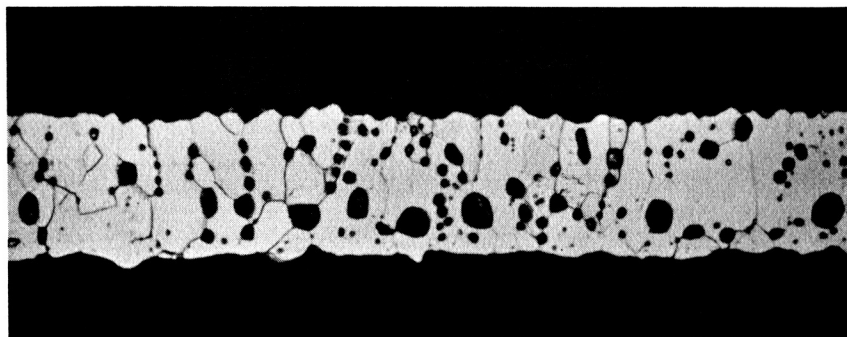
No. 103 Deposited at 895°F (480°C), H_2/WF_6 - 10/1, 49 mm Hg
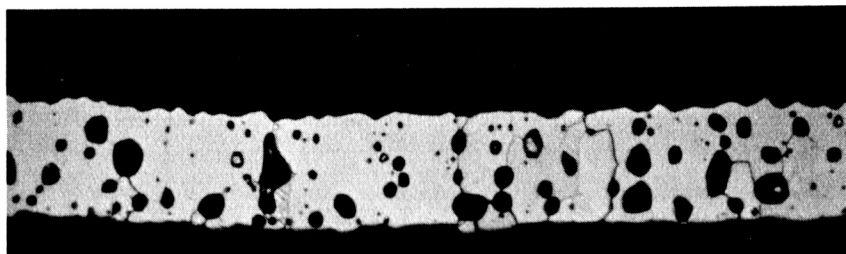
No. 100 Deposited at 895°F (480°C), H_2/WF_6 - 10/1, 4 mm Hg
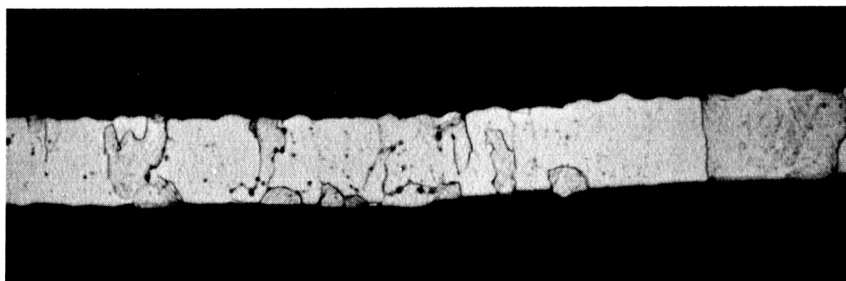
No. 100A Deposited the same as No. 100 . Post Deposition Heat
Treatment: 1 hour at 3600°F (1980°C), 10^{-6} mm Hg.

400X   Murakami's Etchant

FIGURE 36

Free Standing Layers Deposited at 895°F (480°C) After Testing at 4500°F (2480°C)
In Hydrogen for 2 hours.
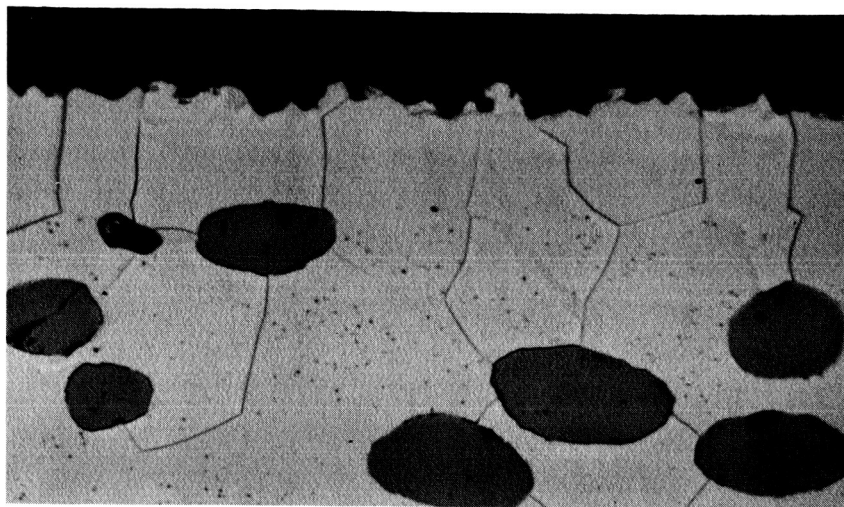
—Cladding

—Original Interface

—Substrate

Deposition Parameters: 1150°F (620°C), H_2/WF_6-33/1, 4 mm Hg
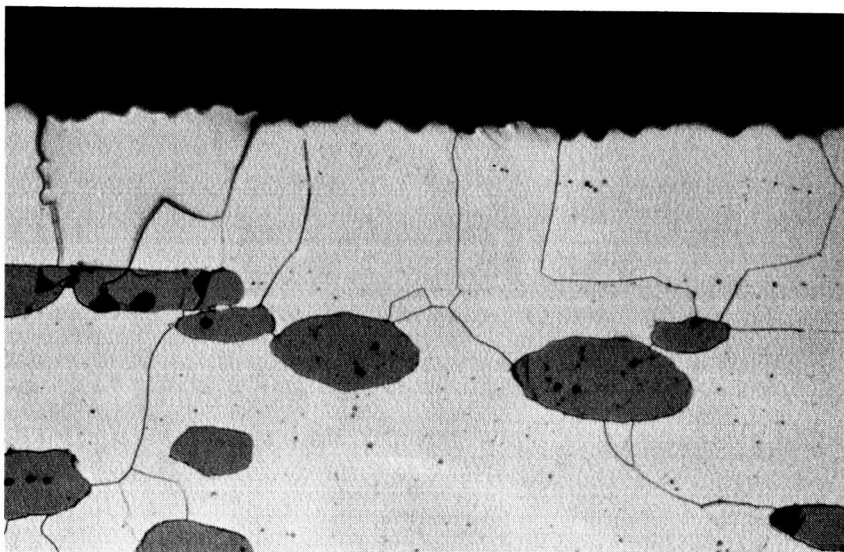
—Cladding

—Original Interface

—Substrate

Deposition Parameters: 1150°F (620°C), H_2/WF_6-10/1, 16 mm Hg

400X   Murakami's Etchant

FIGURE 37

Samples clad at 1150°F (620°C) after testing at 4500°F (2480°C)
in hydrogen for 2 hours.

Astronuclear
Laboratory
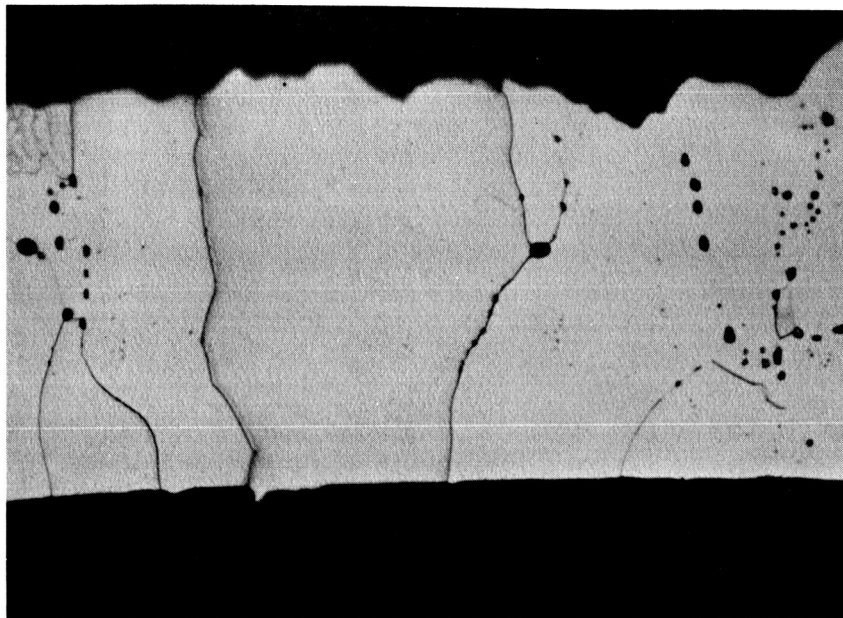
No. 101 Deposited at 1290°F (700°C), H_2/WF_6-10/1, 6 mm Hg
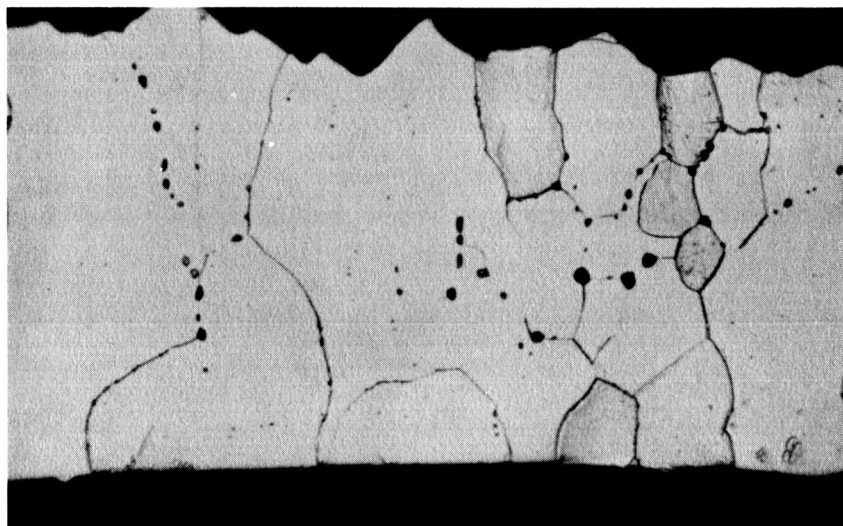
No. 101A Deposited the same as No. 101. Post deposition
heat treatment: 1 hour at 3600°F (1980°C), 10^{-6} mm Hg.

400X   Murakami's Etchant

FIGURE 38

Free standing layers deposited at 1290°F (700°C) after testing at
4500°F (2480°C) in hydrogen for 2 hours.

 Astronuclear
Laboratory

SUMMARY OF RESULTS

Development of methods for chemical vapor deposition of tungsten by the hydrogen reduction of WF_6 to produce tungsten cladding on $W-UO_2$ composites was successful in the goal of limiting UO_2 loss from the substrate at elevated temperature and also resulted in acquisition of much new information. It is, therefore, appropriate to summarize the results.

1. The rate of deposition of tungsten from WF_6 and the uniformity of the deposit can be varied in a predictable and reproducible manner by exercising control over the temperature, pressure, and gas flow rates at which the deposit is made. Deposition rate is most strongly dependent on temperature and pressure; longitudinal uniformity, on deposition rate versus gas flow rate. Both deposition rate and deposit uniformity over a 3-inch length are influenced by deposition chamber geometry. At constant WF_6 flow (cc/min.), deposition rate increases and uniformity is improved as the cross sectional area of the chamber is reduced.

2. The thickness of pyrolytic tungsten deposits can be readily controlled within a total spread of 0.0005" in the 0.0005" to 0.001" range and to within 0.001" in the range 0.001" to 0.005".

3. The density of deposits made over wide ranges of parameters exceeds 98% of the theoretical density.

4. The microhardness of tungsten deposited from WF_6 averages 595 DPH and increases slightly with deposition temperature. Post deposition heat treatment at 3600°F (1980°C) for 15 minutes at 10^{-6} mm of Hg decreases the average hardness to about 465 DPH.

5. With the exception of Cu, C, and F, the level of 26 elements analyzed in vapor deposited tungsten is less than 10 ppm each. Copper, carbon, and fluorine levels are each less than 20 ppm, 33 ppm and 20 ppm respectively.

6. Deposits can be made to grow epitaxially from both tungsten and $W-UO_2$ substrates with excellent adherence by pretreating the substrates in hydrogen at less than 15 mm Hg absolute and 1600°F (872°C) in the deposition chamber prior to coating to reduce surface oxides and provide a clean surface on which the deposit may nucleate. Although adherent substrate nucleated deposits may be produced on $W-UO_2$ composites, the structure of the deposit over UO_2 particles that are exposed to the substrate surface is columnar and non-substrate nucleated.

7. Sectioning clad substrates with an abrasive disc cutter prior to metallographic preparation is an excellent, although somewhat crude, tool to evaluate deposit adherency. If the deposit is non-adherent, separation at the interface invariably occurs.

8. Deposits produced on both unfueled, recrystallized tungsten and on $W-UO_2$ composites exhibit a high enough degree of adherency to survive bend tests at room temperature, 800°F (430°C), and 1000°F (540°C) around a 0.025" radius without separating at the substrate-clad interface.

9.   The structure of tungsten deposits on $W-UO_2$ composites may be altered by recrystallization and bonding may be improved, as a result of grain growth across the interface, by post deposition heat treatment at $3600^\circ F$ ($1980^\circ C$) for 15 minutes in a vacuum of 10^{-6} mm of Hg.

10.   As revealed by fluorescent penetrant inspection, deposits produced over a wide range of deposition rates are free from surface defects and cracks.

11.   Eddy current and pulse echo ultrasonic testing techniques which were utilized in this program were not sufficiently sensitive to detect non-adherent, mechanical bonding at the interface between the vapor deposited tungsten and tungsten substrate.

12.   Deposits produced on substrates directly heated by induction exhibit the same high degree of uniformity, adherency, and substrate nucleation as deposits produced on substrates heated radiantly in a hot chamber. It appears that basic technology developed with hot wall deposition systems may be equally applied to coating directly heated samples in cold wall systems with only minimal additional experimentation being required to establish optimum gas flow and deposit growth rates providing the coil is tuned to the substrate to prevent undesirable temperature gradients in the flowing gas.

13.   Tungsten deposited from WF_6 vapor on $W-20 ^V/o \, UO_2$ composites effectively and consistently restricts fuel loss from the composites to less than 0.15 mg/cm^2 (0.21% of contained UO_2) for times up to 2 hours at $4500^\circ F$ ($2480^\circ C$) in flowing hydrogen.

14.   Vapor deposited coatings on both unfueled tungsten and $W-20 ^V/o \, UO_2$ exhibit microporosity after being tested at $4500^\circ F$ ($2480^\circ C$) in hydrogen for 2 hours, the degree of which is dependent upon deposition parameters and post deposition heat treatment history. Cladding deposited at $1150^\circ F$ ($620^\circ C$) resulted in greatly reducing the amount of microporosity that occurs during subsequent high temperature testing.

15.   Thin layers of tungsten deposited on $W-UO_2$ composite surfaces at $1295^\circ F$ ($700^\circ C$) prior to depositing a thicker, more easily controlled layer at $895^\circ F$ ($480^\circ C$) exhibit virtually no porosity after the high temperature fuel retention test.

16.   Post deposition heat treatment of tungsten clad $W-UO_2$ composites $3600^\circ F$ ($1980^\circ C$) at 10^{-6} mm of Hg for 1 hour significantly reduces the formation of porosity in the clad during 2 hour high temperature testing at $4500^\circ F$ ($2480^\circ C$) in hydrogen for those coatings deposited at $895^\circ F$ ($480^\circ C$).

17.   Removal of UO_2 particles exposed to the surface of the $W-UO_2$ composites by dissolution with HNO_3 prior to cladding deposition offers no advantage to improving fuel retention performance in single cycle tests at $4500^\circ F$ ($2480^\circ C$) in hydrogen.

18.   Trace quantities of zirconium detected in the surface of as-rolled $W-UO_2$ composites do not significantly degrade the vapor deposited tungsten cladding during single cycle high temperature fuel retention testing at $4500^\circ F$ ($2480^\circ C$) in hydrogen for 2 hours.

CONCLUSIONS

The program conducted on the development of techniques for tungsten-cladding of $W-UO_2$ composites by the hydrogen reduction of WF_6 leads to the following conclusions:

1. The feasibility of retaining UO_2 in $W-UO_2$ composites (in the form of thin 3-inch long rectangular plates) at elevated temperature using a highly reliable, well bonded, tungsten cladding produced by the hydrogen reduction of WF_6 has been established.

2. It was demonstrated that crack-free, completely encapsulating, high-purity, tungsten cladding of a predictable and controlled thickness which has essentially theoretical density and which has a pore-free, metallurgical bond to the substrate may be applied to $W-UO_2$ fuel reproducibly.

3. Environmental tests for 2 hours at 4500^oF (2480^oC) in flowing hydrogen demonstrated that the chemical vapor deposited tungsten cladding successfully and consistently limited the loss of UO_2 from the fueled composites to less than 0.15 mg/cm^2 (0.21% of contained UO_2) and retained its good integrity and metallurgical bond.

4. No gross imcompatibility of tungsten clad produced by hydrogen reduction of WF_6 occurred to cause catastrophic loss of UO_2.

5. Tungsten cladding produced by hydrogen reduction of WF_6 exhibits good "throwing power" and the capability of coating complex, multichannel, fuel-shapes with the same integrity as flat plates.

6. Metallographic examination following the high temperature tests, showed that microporosity (due ostensibly to system or fluoride impurities) did on occasion develop along the grain boundaries and bond interface of the tungsten cladding. The extent of this porosity could be controlled to a substantial degree by choosing an optimized cladding deposition temperature.

7. Versatility of the process for uniformly cladding other fueled shapes and sizes was demonstrated by successfully cladding both flat-plate tensile specimens (7-inch length) and thin-wall tubes (1/2 inch diameter x 1 inch length).

RECOMMENDATIONS

1. Little information is presently available that relates the influence of impurities in the grain boundaries of the cladding to the elevated temperature fuel retention performance of clad $W-UO_2$ composites. Since it is desirable that the cladding process be finalized as a reliable, reproducible production method at the earliest possible date, it is recommended that additional experimental work on the control of impurities and their distribution in the cladding be initiated. This work should include defining all elements that might affect elevated temperature fuel retention performance and the method of controlling the source of these impurities in both system construction materials and in processing gases (H_2, Ar, and WF_6).

2. It will be necessary to develop techniques applicable to cladding complex shapes – both for coating relatively long, small cross-section holes and for coating the edges of complex shaped webb sections.

3. There is a need for improved mobile supports which are applicable to both simple and complex shapes.

Astronuclear
Laboratory

REFERENCES

1. Lenz, W. H. and Mundinger, P. R., Studies of Refractory-Metal-UO_2 Fuel Materials, LAMS-2971, January 7, 1964 (Classified Report).

2. Bakish, R., Comments to Powder Metallurgy Materials for Rockets, Missiles and Space Vehicles, Deutsch, G. C., Ault, G. M., Powder Metallurgy in the Nuclear Age, Plansee Proceedings, 1961, Rentte, Tyral, 1962.

3. Brenner, A. and Reid, W. E., Vapor Deposition of Tungsten, U.S. Patent 3,072,983 (to United States of America, Secretary of the Navy), January 15, 1963.

4. Bakish, R., Gellar, C. A. and Marinow, I., Vapor Phase Metallurgy and Ceramics, Journal of Metals, October, 1962.

5. Holzl, R. A., Structural and Containment Properties of Vapor Deposited Tungsten Cladding on Nuclear Fuel Elements at Very High Temperatures, Materials Science and Technology for Advanced Applications, Volume II (1964).

6. Miller, A. and Burnett, G. D., Chemical Vapor Deposition of Tungsten at Low Pressure, Journal Electrochem. Soc. 109, 973-6 (1962).

7. Heestand, R. L. and Leitten, C. F., Jr., Parameters for the Production of Refractory Metal Tubing by the Vapor Deposition Process, Symposia on the Applied Aspects of Refractory Metals, San Francisco, December, 1963.

8. Ellis, W. P. and Roberts, B. W., Fluoride Interference Films on Uranium Dioxide. II. Kinetics of the Hydrofluorination Reaction, Journal of Chemical Physics, Vol. 39, No. 5, 1176-1181, September, 1963.

9. Private Communication, Frederick, C. L., Battelle Northwest, Richland, Washington.

APPENDIX I

Determination of Oxygen-Uranium Ratio
in Surface UO_2 of Rolled Plates of W-20 v/o UO_2

X-ray diffraction measurements were made on the exposed surface UO_2 phase of the W-UO_2 composites to test for the presence of excess oxygen. A reduced lattice parameter of the UO_2 indicates that the oxygen-uranium ratio is greater than 2 to 1.

Measurements were made on a diffractometer with a copper target diffraction tube to measure the 2θ angle in the region from 26° to 60°. Particular attention was paid to the (311) UO_2 peak occurring between 55° and 57°. As a standardizing method to determine the UO_2 composition, a plate was sectioned and 4 or 5 pieces were mounted in plastic metallographic mounting material with the cut edges side by side. A diffractometer trace was taken of this composite surface to determine the composition of the internal UO_2. This trace shows the (311) d-spacing to have a value of 1.6515 (2θ angle of 55.64°) indicating a nearly normal lattice parameter of 5.470 Å. The external surfaces of all the rolled samples were then scanned and the resultant UO_2 d-values compared with that obtained for the internal UO_2 particles. The tungsten peaks in all cases were used as a standard check of goniometer alignment.

The diffractometer patterns from the surface UO_2 of all samples showed the same cubic structure as the interior UO_2, but the calculated lattic parameters for the surface particles were smaller than that obtained for the interior UO_2 particles indicating excess oxygen present in the lattice of surface UO_2. It should also be mentioned that it is possible for other contaminants to similarly reduce the lattice parameters as indicated in the body of the report.

Astronuclear
Laboratory

TABLE A-1

Bend Test Results for Tungsten Coated Samples

Test Temperature (°F)	Type of Sample	Deposition Temperature (°F)	Bend Angle (°)	Maximum Stress (psi)	Remarks
R.T.	W on W	996	--	---	Brittle
R.T.	W on W-UO$_2$[1]	896	--	---	Brittle
800	W on W[1]	1022	34	80,500	
800	W on W	842	4	76,000	
1000	W on W	662	114	107,000	Bent without fracture.
1000	W on W-UO$_2$	896	25	55,000	
1000	W on W-UO$_2$[1]	896	30	40,500	After 2 hrs at 4500°F.
1000	W on W-UO$_2$[1]	1292+896	4	65,000	Fracture stopped.

[1]Microstructure shown in Figures 20 through 22.

TABLE A-II
CLADDING THICKNESS DATA
FOR 1/32" x 3/4" x 3" W-UO$_2$ PLATES[1]

Substrate Type	Sample No.[2]	Desired Cladding Thickness (mils)	Cladding and Actual Thickness Range (mils)	Wt. gms. Before	After
A	130-1	0.5-1.0	0.75-1.0	12.44374	13.45748
A	130-2	0.5-1.0	0.5 -1.0	12.51378	13.26166
A	158-1	0.5-1.0	0.75-0.9	12.80077	13.82064
A	158-2	0.5-1.0	0.7 -0.95	12.68300	13.76360
A	1-3 [3]	1.0-2.0	1.35-2.0	---	---
A	159-1	1.0-2.0	1.4 -1.8	12.35354	14.23273
A	160-2	1.0-2.0	1.6 -1.65	12.61338	---
A	167-1	1.0-2.0	1.65-1.9	12.64251	---
A	159-2	4.0-5.0	4.0 -4.5	12.49640	17.99447
A	160-1	4.0-5.0	3.8 -4.25	12.42607	17.26178
A	168-1	4.0-5.0	4.1 -4.3	12.36175	---
A	168-2	4.0-5.0	3.8 -5.0	12.53595	---
B	118-1	0.5-1.0	0.7 -0.95	12.17554	13.18162
B	118-2	0.5-1.0	0.55-1.1	12.17154	13.58216
B	119-1	0.5-1.0	0.4 -0.9	12.60427	13.42125
B	171-1	0.5-1.0	0.55-0.9	---	---
B	117-1	1.0-2.0	1.6 -2.0	12.37845	14.34705
B	117-2	1.0-2.0	1.3 -2.0	12.72690	14.26372
B	128-1	1.0-2.0	1.8 -2.1	12.51731	---
B	128-2	1.0-2.0	1.1 -1.8	12.53932	---
B	122-1	4.0-5.0	4.1 -4.7	12.51619	---
B	123-2	4.0-5.0	3.9 -4.8	12.27142	---
B	166-1	4.0-5.0	4.2 -4.4	12.50337	---
B	170	4.0-5.0	4.3 -4.8	---	---

Astronuclear
Laboratory

TABLE A-II (Continued)

Substrate Type	Sample No.	Desired Cladding Thickness (mils)	Cladding and Actual Thickness Range (mils)	Wt. gms. Before	After
C	124-1	0.5-1.0	0.8 -1.0	12.48826	13.48363
C	124-2	0.5-1.0	0.5 -0.7	12.56155	13.25676
C	127-1	0.5-1.0	0.8 -1.0	12.35473	---
C	129-1	1.0-2.0	1.6 -1.7	12.47721	---
C	129-2	1.0-2.0	1.3 -1.6	12.54536	---
C	161-1	1.0-2.0	1.7 -1.8	12.87859	---
C	167-2	1.0-2.0	0.9 -1.5	12.56025	---
C	169-1	4.0-5.0	4.15-5.0	---	---
C	161-2	4.0-5.0	4.3 -4.8	12.44684	---
C	126-1	4.0-5.0	4.1 -4.9	12.44888	---
C	126-2	4.0-5.0	4.0 -4.6	12.18767	---
C	127-2	0.5-1.0	0.4 -0.9	12.58375	---

1. Samples were supported as in Figure 2D in a resistance heated muffle.
2. The deposition parameters for these samples were $1150^{\circ}F$ $(620^{\circ}C)$, H_2/WF_6-10/1, pressure <10 mm Hg.
3. This sample was coated in the RF induction heated chamber.

Astronuclear
Laboratory

TABLE A-III

CLADDING THICKNESS DATA FOR W-UO$_2$ TENSILE SPECIMENS[1,2,5]

Substrate Type	Sample No.	Run No.[3]	Cladding Thickness (mils)	Wt., gms Before	Wt., gms After
A	1	140[4]	1.5-1.7	25.59478	--
A	2	142[4]	1.0-2.0	25.47911	29.43954
A	3	145[4]	1.0-1.5	24.50522	--
A	4	147	1.5-2.0	25.58977	29.68104
A	5	149	1.4-1.9	25.41149	29.59689
A	6	155[4]	1.0-2.0	24.81637	--
A	7	153	1.5-2.0	24.88173	28.82257
A	8	151	1.0-2.0	24.92810	29.29631
B	1	157	1.1-1.7	25.34414	29.47890
B	4	138[4]	1.0-1.5	29.21036	--
B	5	137	1.4-1.7	24.71897	28.83038
B	6	136	1.4-1.7	25.05684	29.01363
B	7	135	1.3-1.7	24.95502	28.79672
B	9	133	1.4-1.7	23.57785	27.13614
B	10	132[4]	1.2-1.8	23.15970	--
B	11	131	1.0-1.7	25.39361	28.89356
C	1	143	1.1-1.9	25.06285	28.72152
C	3	146	1.5-1.8	25.61851	29.57332
C	4	148	1.6-1.7	25.60956	29.36029
C	5	150	1.6-1.7	25.49127	29.42667
C	6	152[4]	1.2-2.0	24.78304	--
C	7	154	1.7-1.9	24.93637	29.00716
C	8	156	1.2-1.6	25.10323	28.74579
C	2	144	----	Broke during processing	

1. W-UO$_2$ tensile specimens were 7" x 0.75" x 0.020"

2. Samples were supported as in Figure 2D in a resistance heated muffle.

3. The deposition parameters for these runs were 1150°F (620°C), H$_2$/WF$_6$-10/1, pressure < 10 mmHg.

4. Rework on these samples were done by using RF induction heating.

5. Desired cladding thickness - 1.0 to 2.0 mils.

DISTRIBUTION LIST

NASA Lewis Research Center (3)
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: Robert M. Caves

NASA Lewis Research Center (1)
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: Technical Utilization Office
                      MS 3-16

NASA Lewis Research Center (2).
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: Library

U. S. Atomic Energy Commission (3)
Technical Reports Library
Washington, D. C.

A.E.C. Headquarters (1)
Div. of Reactor Development
Washington, D. C.
Attention: S. Christopher

National Aeronautics & Space Administration(1)
Washington, D. C.   20546
Attention: NPO

NASA Lewis Research Center (1)
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: Office of Reliability and Quality
                      Assurance

NASA Ames Research Center (1)
Moffett Field, California 94035
Attention: Library

NASA Goddard Space Flight Center (1)
Greenbelt, Maryland   20771
Attention: Library

NASA Langley Research Center (1)
Langley Station
Hampton, Virginia   23365
Attention: Library

NASA Lewis Research Center (1)
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: John J. Fackler
                      Contracting Officer, MS 54-1

NASA Scientific & Technical Information
  Facility (6 & Reproducible)
Box 5700
Bethesda, Maryland
Attention: NASA Representative

NASA Lewis Research Center (1)
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: Reports Control Office

U. S. Atomic Energy Commission (3)
Technical Information Service Extension
P. O. Box 62
Oak Ridge, Tennessee

National Aeronautics & Space Administration (1)
Washington, D. C.   20546
Attention: G. Deutsch

NASA Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio   44135
Attention: (One copy to each)
      Nuclear Rocket Technology Office, MS 54-1
      Neal Saunders, MS 105-1
      S. Kaufman, MS 49-2
      T. Moss, MS 500-309
      J. Creagh, MS 500-309
      H. Smreker, MS 54-1

NASA Flight Research Center (1)
P. O. Box 273
Edwards, California   93523
Attention: Library

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California   91103
Attention: Library

Distribution List (continued)

NASA Marshall Space Flight Center (1)
Huntsville, Alabama   35812
Attention: Library

NASA Manned Spacecraft Center (1)
Houston, Texas   77001
Attention: Library

Argonne National Laboratory (2)
9700 South Cass Avenue
Argonne, Illinois
Attention: J. Schumar
             R. Noland

NASA Western Operations (1)
150 Pico Blvd.
Santa Monica, California   90406
Attention: Library

Oak Ridge Gaseous Diffusion Plant (1)
Oak Ridge, Tennessee
Attention: P. Huber

Hanford Laboratories (1)
Richland, Washington
Attention: F. Albaugh

Battelle Memorial Institute (1)
505 King Avenue
Columbus, Ohio
Attention: E. Hodge

General Electric - NMPO (1)
P. O. Box 15132
Evendale, Ohio   45215
Attention: J. McGurty

Sylvania Electric Products (1)
Chemical and Metallurgical Division
Towanda, Pennsylvania
Attention: M. MacInnis

Nuclear Materials & Equipment Corporation
Apollo, Pennsylvania
Attention: B. Vondra

United Nuclear Corporation (1)
New Haven, Connecticut
Attention: E. Gordon

Westinghouse Electric Corporation (1)
Astronuclear Laboratory
P. O. Box 10864
Pittsburgh, Pennsylvania 15236
Attention: D. Thomas

General Atomic Division (1)
General Dynamics Corporation
P. O. Box 608
San Diego, California   92112
Attention: A. Weinberg

Union Carbide Corporation (1)
Nuclear Products Department
Lawrenceburg, Tennessee
Attention: W. Eatherly

Minnesota Minning & Manufacturing Co. (1)
Nuclear Products Department
St. Paul, Minnesota
Attention: J. Ryan

Atomics International Division (1)
North American Division
8900 Desota Avenue
Canoga Park, California
Attention: S. Carneglia

General Electric Company
Vallecitos Atomic Laboratory
P. O. Box 846
Pleasanton, California
Attention: Dr. A. Kaznoff

Martin - Marietta Corporation
Nuclear Division
Baltimore, Maryland   21203
Attention: C. Eicheldinger